

POLYTHENE

THE TECHNOLOGY AND USES OF
ETHYLENE POLYMERS

CFTRI-MYSORE



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2. pigmentation
3. molecular structure
4. mechanical properties
5. physical testing
6. polythene specifications
7. screw design
8. dies.
9. industrial piping
10. chemical plant

TLWS



POLYTHENE

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THE TECHNOLOGY AND USES OF ETHYLENE POLYMERS

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PREFACE

THE emergence of polythene as one of the most important of the plastics materials, at least in terms of tonnage, has been a major feature of the plastics industry in recent years. The great deal of technical work which has gone into its development now makes a critical appraisal of the available data desirable. The present volume, which has been designed to meet this need, is made up of a number of specialized contributions on the various aspects of polythene, theoretical, technological and marketing, written by experts from the United Kingdom and the U.S.A.

Since the book was first conceived, much interest has been aroused by the newer high density types of polythene. These have not been treated as a separate class of materials but have been described or examined where they are relevant in each chapter. The terms "high density" or "low density" have been adopted rather than "high pressure" or "low pressure" because, obviously, a property characteristic is more descriptive than a method of manufacture. It is true that classification of the newer materials by terms such as "linear" or "degrees of stiffness" could also have been adopted, but it seemed to the editors that density was the simplest characteristic to use. Where "polythene" appears unspecified it refers to low density material.

The terms "melt index" or "melt flow index" (and occasionally "M.F.I.") have been used according to the individual choice of the authors; either of these terms is preferable to the old grade number, and is more specific. Although the term "polyethylene" is common in the U.S.A. and in Europe, "polythene" has been used throughout this book because this was the generic term originally adopted in the United Kingdom by its inventors. Furthermore, the British Standards Institution and the British Plastics Federation have both adopted "polythene" as the preferred term. It is, of course, a popular misconception that "polythene" is a trade mark.

In volumes of this nature there is always the difficulty of overlapping from one chapter to another as authors are not always aware of what has been written in other chapters. This overlapping has, on occasion, been deliberately retained because it seemed to the editors that as far as possible chapters should be complete within themselves, and some repetition has been allowed to save the reader from constant cross referencing. This is particularly obvious, for example, in discussions on environmental cracking and weathering which are referred to in several chapters, but of course from different viewpoints.

Finally, the editors would like to express their gratitude to D. E. Strain, of E. I. du Pont de Nemours & Co. Inc., who has made many constructive suggestions. The editors would also like to thank P. C. Allman, who undertook the laborious but vital work of indexing.

A.R.

P.M.

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PART I

MANUFACTURE AND PROPERTIES

CHAPTER I

THE HISTORY OF POLYTHENE

J. C. SWALLOW

ALTHOUGH a minute amount of a solid polymer of ethylene was made in the Research Department of the Alkali Division of Imperial Chemical Industries Limited in March 1933 and recognized as such, it was not until December 1935 that eight grams of the material were made in small-scale apparatus and the decision taken to proceed with the development of the material. Therefore this substance, described under the generic name of polythene in England, is now twenty-one years old, and it can truly be said that no other modern plastics material has developed in so spectacular a manner, production plans in the world today being approximately 760,000 tons.

The history of any chemical discovery and its subsequent development is always of interest, especially at the present time when so much thought is being given to the organization of industrial research. As time passes any story tends to become idealized and presented in a way which suggests a steady and logical growth from the start of the research programme to the discovery and development of the particular product. The story of polythene however provides an unusually clear-cut instance of the unexpected results that may come from research, and of the importance of the role of chance in such work. The actual history of the development can be separated into several distinct phases. Between 1931 and 1935 the study of the effects of very high pressures on chemical reactions was being actively pursued, and arising from this work the discovery of polythene was made. In the years 1935 to 1939 a manufacturing process was devised and particular uses for which the product was uniquely suitable were developed. Between 1939 and 1945 attention was principally given to the production of the material in the U.K. and U.S.A. specifically for the high frequency applications in radar cables and ancillary equipment for wartime uses, and during this period the other uses which have come to the forefront today were scarcely investigated at all. Lastly, in the period from 1945 to the present time polythene has been developed as a plastics material in its own right and has found large tonnage applications in mouldings, films and cable coverings.

THE DISCOVERY

The actual history of polythene began in 1932 at Northwich, Cheshire, in the Alkali Division of ICI, when M. W. Perrin and the author of this Chapter recommended that work on the effect of very high pressures on

chemical reactions should be carried out. In their report, the published work on the predominantly chemical effects of high pressure was examined and also the theoretical reasons for expecting that pressure should influence a chemical reaction. Experimental work which had been published was examined in the light of these theories, and particular emphasis was placed on the work of P. W. Bridgman at Harvard, and on the work of J. B. Conant who had studied some organic reactions in the liquid phase up to pressures of 20,000 atms. This work showed that polymerization reactions were markedly affected, and Conant reported the formation of unknown polymers of butyraldehyde when this chemical was subjected to pressure of 12,000 atms. for 40 hours. This result, together with Bridgman's observation that an allotropic form of phosphorus which could not be synthesized by other means had been made at a pressure of 12,000 atms. and 200°C., inspired some confidence in the hope that really novel effects were to be discovered.

A number of reactions of interest were proposed by the Dyestuffs Division of ICI. which were in fact not selected because they might be expected on theoretical grounds to be markedly affected by pressure; rather it was hoped that compounds not normally reactive might become so, or that at high pressures reactions which normally need vigorous catalysts might occur without them.

The design of the apparatus used for liquid reactions was largely based on the equipment used by Professor Michels in Amsterdam University, in whose laboratory a number of the staff of the project had worked, and this enabled studies to be made up to 3000 atms. and up to 200°C. Some fifty reactions were tried during 1932 and 1933, and the results were all disappointing. Some of the reactions suggested were gaseous reactions and some involved gas-liquid reactions. Amongst the latter was the reaction between ethylene and benzaldehyde, which was tried in March 1933, at 170°C. and with an ethylene pressure of 1400 atms. The walls of the vessel were found to be coated with a thin layer of a "white waxy solid" to quote from the notebook of R. O. Gibson who carried out the experiment. The solid was recognized as a polymer of ethylene, but on repeating the experiment with ethylene alone the ethylene decomposed with great violence to give hydrogen and methane, whilst the reaction vessel was filled with amorphous carbon. The decomposition caused a rapid rise in pressure and led to bursts in the joints, tubes and gauges of the apparatus, and it was decided not to pursue this investigation until more suitable apparatus had been devised.

Whilst thought was being given to the problems of design of liquid and gas compressors for the pressure range above normal industrial practice, other reactions were examined including the effect of pressure on the polymerization of linseed oil which at that time appeared to have promise of technical value in the properties of the polymerized oil obtained. Considerable work was also carried out on the kinetics of the effect of pressure on liquid reactions, in order to obtain some understanding of the nature of pressure effect on the rate, and this work

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afforded a valuable background for the subsequent research on the polymerization of ethylene.

In May 1935 the results of the high pressure work were critically examined and it was decided to carry out further experimental work, with the improved apparatus then available, on the polymerization of ethylene. Improvements in technique in the layout of the laboratory made such work very much easier, and in December 1935 the polymerization was again tried in an 80 cc. vessel supplied with ethylene from a semi-automatic gas intensifier. When the temperature reached 180°C . the pressure began to fall and was raised to its original value, after which the pressure was released, the vessel dismantled, and a total weight of eight grams of white powdery solid was extracted.

Polymerization had certainly not accounted for all the pressure drop during the experiment, and there must have been a leak at one of the joints in the apparatus, and here again the element of chance played an important role, and it took some months of intensive work by all those in the research team to elucidate the full reasons as to why, if the leak had not occurred, the experiment would probably have been far less spectacular than it was, and might have been a repetition of the earlier ones.

The success of the experiment in December was in fact due to the additions to the reaction vessel of fresh ethylene to replace that which had leaked out. This ethylene contained by chance about the right amount of oxygen to catalyze the formation of successive amounts of the polymer.

Some time prior to this work Professor Michels had been asked to devise a small-scale continuously operating compressor for handling gases up to 3000 atms. and in 1936 this ingenious piece of equipment was delivered which worked on the principle of hydraulically operated mercury pistons. At that time no design was available for a compressor to operate above 1000 atms., the highest pressure used in chemical industry, nor did the designers of compressors show any eagerness to construct prototype equipment for such a pressure range. It would therefore truly be said that the devising of a continuous process at that time would not have been possible without this piece of equipment.

The polythene prepared in December 1935 was found to melt quite sharply at about 115°C . and the molten polymer could be drawn out into filaments which on stretching exhibited the phenomenon of "cold drawing"; that is, the thread elongated at constant stress and showed a shoulder between the undrawn and the drawn material. This phenomenon had been observed by W. H. Carothers¹ of du Pont as a property of polyesters and polyester amides, and indicated that this solid polymer of ethylene was a reasonably straight chain polymer of fairly high molecular weight.

MANUFACTURING PROBLEMS

The first problem, therefore, which faced the research team at that time, assuming the material had some industrial use, was the development of a process in which the heat of a highly exothermic polymerization

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reaction could be dissipated and the product removed from the high pressure container in which it was formed. It was obvious that to do this on a practical scale meant the devising of a continuous polymerization system in which the heat of reaction could be removed in a controlled manner. The second problem, assuming the latter could be successfully carried out, was to find a use or uses in which the particular combination of properties possessed by polythene would be of practical value.

As regards the process, one of the natural choices was a tubular reactor in which the velocity of the gas through the tubes was such that a high heat transfer could be maintained and the heat extracted through the walls of the tube. A second method was to introduce some liquid into the reaction mixture which whilst not affecting the polymerization reaction in any way, would absorb the heat of reaction through the latent heat of the liquid. A third was to remove the heat of reaction by means of the difference in the total heat of the ingoing gas and the outgoing polymer and residual gas, and to operate in an autothermal manner. All three methods and variations thereof have been employed by the various manufacturers of polythene in different countries, and were devised in the interests of chemical engineering simplicity, and with a view to getting the maximum output from a given high pressure volume whilst maintaining steady polymerization conditions. It is now recognized that quite small variations in the molecular structure of polythene can be of technological importance in the various uses to which the product is put. The effects of the process used on the structure of polythene produced by it have therefore become of greater importance.

FIRST EVALUATIONS

Much is written, today, on the way in which a new product should be developed with a view to shortening the time between its discovery and its large-scale production and commercial availability. To use the phraseology of today it would have been difficult at that time to have carried out a "Market Survey" which would have led to any profitable conclusion, but here again the role of chance played a part. It so happened that J. N. Dean of Telegraph Construction and Maintenance Company, who were associated with the production of submarine telegraph and telephone cables, recognized the possibilities of polythene for the insulation of under-water cables, and expressed great interest in examining the material even though it was only available in very small quantities. Another fortunate occurrence was the fact that B. J. Habgood of the Dyestuffs Division of ICI pointed out at a very early stage the similarity of the mechanical properties of polythene to those of gutta percha, a natural material the properties of which were not generally known outside the submarine cable industry. It was therefore decided to concentrate development work on the possible uses of polythene in submarine cable technology, and in this case the economics appeared to be favourable. This arose from the fact that natural gutta percha, suitably purified, had been used as a general insulant for telegraph

cables since 1856, but the introduction at that time of submarine telephone cables required the use of an insulator with lower electrical power loss at the high frequencies employed. Such a material had been devised by the Bell Telephone Company, known as "paragutta" and consisting of a mechanical mixture of purified gutta percha, deproteinized rubber and paraffin wax. This compound was neither cheap nor in fact ideally suited for deep sea cables, and was in fact inferior to polythene mechanically and electrically.

In the small pilot plant that had been erected in the laboratory sufficient material was made and extruded into a mile length of submarine cable to be laid between the Isle of Wight and England by the Telegraph Construction and Maintenance Company. The extrusion equipment normally used for gutta percha was by no means ideally suited for the making of this cable, since the temperatures used with gutta percha are considerably lower than those required for polythene with a melting point 60°C. higher, and in fact at that time there was no commercial extrusion equipment available which was suitable for extruding polythene at all. In spite of these very considerable technical difficulties, the length of cable was successfully made and found to come up to technical expectation, and the experience gained in the making of this cable proved to be invaluable in the quick developments in the making of high frequency cables for radar use a few years later.

On the basis of the estimated requirements for submarine telephone cables it was recommended that a plant should be erected of a few hundred tons per year capacity, and this came into operation in September 1939 on the same day that the Germans invaded Poland. The ethylene for this plant was made by the dehydration of alcohol, and special pains were taken to ensure that it was of the necessary purity for the polymerization reaction. Today the ethylene used for polythene manufacture is made almost entirely from the cracking of natural gas or by the large scale cracking of oil.

The development of uses for polythene, therefore, up to 1939 had been primarily concentrated on the application in submarine cable technology, and little attention was paid to other outlets. It had been suggested that the material might find outlets in cotton reels, golf ball covers and the cases of sporting cartridges, and a certain amount of film had been made by extrusion, although little interest was shown in the material. A considerable amount of interest, however, had been aroused in the cable industry by the advent of polythene, and there was a general feeling that it might well be the ideal insulant for super tension power cables. Since that time cables up to 15,000 volts have been successfully made from polythene, but the original hope for the material in very high voltage cables up to 66,000 volts has not yet been realized. It was considered at the time by cable makers that, since polythene was a hydrocarbon with negligible water absorption and low power factor, it should be ideal for this purpose, and would probably have the necessary high voltage breakdown characteristics. Subsequent work showed that there

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was no fundamental reason for believing that polythene should have a very high breakdown voltage compared with other plastics. The high thermal expansion coefficient of polythene, and the difficulty of avoiding voids when the cable is flexed, proved to be the principal difficulties which have never been satisfactorily overcome.

WAR TIME DEVELOPMENTS

Looking back, therefore, on the policy of development which was adopted at that time it turned out in the event to be very successful. Submarine cables insulated with polythene were not laid until the end of the war, when they formed a link between England and France during the latter part of the European battles. At the beginning of the war the need arose almost immediately for flexible high frequency cables for ground and air-borne radar equipment. The small plant which came into operation in 1939 was soon found to be too small, and a larger unit was erected in Cheshire by the Alkali Division in which it was possible at that time only to scale up the existing equipment to produce a larger quantity of product. By the time the war had started it was possible to control the molecular weight of polythene in a continuous polymerization process, and the method of characterizing the product for technical use, which is still largely used today, was the measurement of the liquid viscosity of the polymer at 190°C. at a given rate of shear. The apparatus is still known as the "grader".

The grade which had been originally used for submarine cable insulation presented considerable difficulties in the type of extrusion equipment available at that time in the U.K. and use was therefore made of a discovery by E. G. Williams that polyisobutylene of molecular weight of approximately 100,000 could be used as a plasticizer to give the material a wider plastic range, and at the same time conferring on the polythene lower temperature flexibility, an important property for use in air-borne radar cables. Furthermore, it was easier with such a mixture to ensure concentricity in the thicker cables than with polythene alone because of the greater plastic range of such a mixture. This practice of using 12½–15% polyisobutylene was continued throughout the war until it was necessary to produce cables with higher temperature resistance, for which polythene of higher molecular weight was used. U.S. practice, once polythene manufacture had started in that country, was to use a higher molecular weight material from the beginning, rather than mixtures with polyisobutylene, but the extrusion equipment available in the U.S. was more suitable for use at higher temperatures with the higher liquid viscosities of the higher molecular weight polythenes. In 1941 the information on polythene manufacture and the use of the material in radar equipment was communicated to the U.S. and du Pont erected a plant in Belle, West Virginia, for making polythene for the Bureau of Ships for the insulation of radar equipment.

A word here should be said about the activities of the Union Carbide & Carbon Corporation who have played such a very great part in the

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world development of polythene in the last ten years. During the war they also put up a plant for production for the Bureau of Ships' requirements, and today they are the largest manufacturers of polythene in the world. A tribute should be paid to this company who throughout have shown a steady belief in the product and its future; as soon as wartime restrictions ended, they immediately extended their manufacturing facilities, thus making the material available in quantity, which led to the development of new and unsuspected large tonnage uses such as film and mouldings.

The significance of polythene in radar equipment is perhaps best illustrated by the words of Sir Robert Watson Watt, the discoverer of radar, in August 1946:—

“The availability of polythene transformed the design, production, installation and maintenance problems of airborne radar from the almost insoluble to the comfortably manageable. Polythene combined four most desirable properties in a manner then unique. It had a high dielectric strength ; it had a very low loss factor even at centimetric wavelengths; it could fairly be described as moisture-repellent; and it could be moulded in such a way that it supported aerial rods directly on watertight vibration-proof joints backed up by a surface on which moisture films did not remain conductive. And it permitted the construction of flexible very high frequency cables very convenient in use. A whole range of aerial and feeder designs otherwise unattainable was made possible, a whole crop of intolerable air maintenance problems was removed. And so polythene played an indispensable part in the long series of victories in the air, on the sea and on land, which were made possible by radar.

“Polythene was an essential element in that ‘single technical device’ to which the Führer ascribed the ‘temporary’ (but as it proved, enduring) set-back experienced by his U-boats.

“It made its contribution to the major naval combats typified by the action in which, as the Commander-in-Chief said, radar enabled the Home Fleet to ‘*find, fix, fight and finish the Scharnhorst*’. It had its part in such continuing operations of the smaller naval crafts as were delightfully summarized in one report ‘Our M.T.B.s were enabled to detect the convoy, retire for a conference while they plotted enemy course and speed, deliver a deliberate and successful attack unobserved, and retire unscathed with the enemy still in doubt as to what had hit him’.

“It had its vital place in the small batch of sets of anti-U-boat airborne radar equipment which, with their shipborne counterparts—also polythene aided—permitted the sinking of a hundred U-boats within a very few weeks.

“And centimetric aerial systems in polythene moulding multiplied the effectiveness of our bomber force by a very large factor indeed; the ruins of Hamburg and Berlin are a monument to a co-operation in which polythene played a great part.

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“It is most fitting that the story of how polythene came—a story to which the overworked adjectives ‘romantic’ and ‘dramatic’ fairly apply, should have several chapters in common with the story—impressive, dramatic and perhaps not short of majestic—of that radar to which Admiral Doenitz has paid an unwilling but most handsome tribute. . . .”

POST WAR DEVELOPMENTS

The two most important post-war developments were the large scale manufacture of film from polythene and its incursion into the moulding industry. One of the early uses for film in the U.K. was the packing of Mepacrine—an anti-malarial drug for the troops in the East—using equipment originally designed for Cellophane. In the U.K. the market for film developed slowly because there was no important demand for a new packaging material: in the U.S.A., on the other hand, with its active packaging industry and its big polythene plants, advances were spectacular. The elegant bubble method of extruding film was developed on a commercial scale together with adequate methods for printing and heat sealing. Within a few years polythene film was extruded in every major industrial country and polythene manufacturers were competing to supply a film grade which would combine clarity with strength and freedom from “blocking”, the technical jargon for the sticking together of polythene films. Today at least one third of all the polythene manufactured in the world is used for the extrusion of film and the market is expanding rapidly.

During the war radar components were moulded from polythene but it was many years before the possibility of moulding large articles was realized. Small ones came fairly quickly but it was not immediately apparent that washing-up bowls or potato baskets, to give two examples, could be injection moulded economically. The idea probably started in the U.K. and caught on rapidly as bigger and bigger injection presses, mostly of U.S.A. origin, became available. Today, at the end of 1956, mouldings rival film as a market for polythene.

Other important developments were the blowing of bottles and the coating of paper, both techniques for which polythene is particularly suitable.

One of the results of the Anti-Trust Judgment in the U.S.A. courts against ICI and du Pont was the compulsory licensing of the ICI master patent² to several important American companies, most of whom are now, at the end of 1956, manufacturing to capacity.

DEVELOPMENT OF HIGH DENSITY POLYMERS

To return to the history of the product itself, C. W. Bunn³ had shown that polythene was not entirely crystalline and that its crystallites were less than 100 Å in diameter and therefore smaller than the average molecule which contained more than 1000 carbon/carbon atoms each

about $1\frac{1}{2}$ Å long. It was supposed that the crystallites were tied together by molecules which both composed them yet passed through them, existing in an amorphous state in the intervening connecting regions. This appeared to explain the partial crystallinity especially at a time when there was no known highly crystalline paraffin of molecular weight comparable to that of polythene. It was readily accepted not only that the peculiar mechanical properties could be attributed to the partial amorphous structure, but also that incomplete crystallinity was to be expected of extremely long molecules, simply because it seemed improbable that in such a very viscous system readjustment during crystallization by cooling could proceed freely enough for every part of every molecule to join in an ordered array. In other words, polythene appeared to fit in well with the fringe/micellar theory of that time of the structure of crystalline polymers.

Until 1940 polythene was therefore regarded as a purely linear long chain hydrocarbon when Fox and Martin⁴ in England by infra-red studies found more methyl groups in polythene than could be accounted for as terminal groups of linear paraffinic molecules. From then on the influence of short or even long branches of the individual chains had to be taken into account in the understanding of the mechanical properties of the polymer. It was not long before it was appreciated that if the chain branching was increased, as it could be by altering the conditions of synthesis to favour the branching reaction, then the properties of the polymer changed in the direction of a less crystalline material of lower density. The early belief that crystal texture controls the properties of the solid polymer was confirmed by other ICI workers, namely Buckley, Cross and Ray,⁵ who examined polymethylenes made from diazo methane by Leitch and Cambron's method.⁶ These products, which are presumably formed by the grouping up of $-\text{CH}_2-$ groups were found to be mainly of higher molecular weight than polythene, but their methyl content was shown to be negligible. Polymethylenes which were the most linear long chain hydrocarbons made up to that time were found to be much less flexible and extensible than polythene, and much more crystalline.

When, therefore, Phillips Petroleum Co.⁷ succeeded in making polythene with a density of 0.96, its physical properties came as no surprise to those conversant with the relationship between the structure and physical properties of long chain hydrocarbons. The Ziegler⁸ polythene, with a density of 0.94, is intermediate in properties as it is in density between low density polythene and the Phillips polythene. Early in 1956 it was announced by ICI that polythene with a density of about 0.94 had been prepared by the high pressure process and that the properties of the material were similar to those of the Ziegler polymer.

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CHAPTER 2

RAW MATERIALS AND MANUFACTURING PROCESSES

F. STEADMAN

THE raw material for polythene is substantially pure ethylene. While some substances interfere with the polymerization process or modify the properties of the product to such an extent that they must be entirely removed, there are other substances whose main effect is that of dilution, leading to increased polythene production costs. The necessary degree of purity with regard to these latter substances is determined by the balance between the cost of their removal from the ethylene and the increase in polymerization costs caused by them.

Ethylene is a hydrocarbon gas of about the same density as air. At atmospheric pressure it boils at -104°C . Ethylene does not anywhere arise naturally, or as a by-product of other large scale operations in a pure form. It does occur as a by-product highly diluted with other gases, or it can be produced deliberately by chemical processes, though again it is usually too impure for direct use for polythene manufacture. A combination of these sources is also possible in which the separation of deliberately manufactured ethylene is combined with the extraction of further ethylene present in dilute form.

The impurities in "raw" ethylene consist of a mixture of gases and vapours which can be removed by chemical means, fractional distillation, or a combination of both. The removal of these impurities is the major obstacle in obtaining ethylene for polythene manufacture.

The suitability of any method of manufacture for a given ethylene requirement must depend on geographical considerations, on the price and availability of raw ethylene, on the cost of gas separation, the requirements of ethylene for other purposes and the value to be put on the other products of the ethylene production process.

On the smallest scale of manufacture the most economic source of ethylene is the chemical dehydration of ethyl alcohol. This is a simple process of low capital cost per ton/year of ethylene, even at the small scale of only a few thousand tons a year. There are two recognized catalysts for the process. Phosphoric acid impregnated coke gives ethylene of sufficient purity, after certain impurities have been removed either by a water scrubber or a carbon absorption plant, for it to have been used directly for polythene manufacture, but improvement in polythene quality has made the use of such gas no longer advisable. The use of alumina as a catalyst gives ethylene more economically than coke and phosphoric acid, but only 97% purity, which cannot be used directly

for polythene manufacture, although it can be used for all the other important industrial purposes of ethylene.

Ethylene can be produced by the hydrogenation of acetylene but this is not considered an economic route to ethylene on the industrial scale.

The first serious attempt to utilize dilute by-product ethylene was the large scale experiment made at Skinningrove, Yorkshire, England, in 1919-21. Coke oven gas containing only about 2% by volume of ethylene was scrubbed with sulphuric acid and ethyl alcohol was recovered from hydrolysis of the ethyl hydrogen sulphate formed. The process was abandoned owing to the large volumes of gas which had to be handled, the poor efficiency of recovery of ethylene from gases at such dilution and the presence of other constituents of the gas which reacted with the sulphuric acid. Much more recently the deliberate enrichment of coke oven gas for ethylene manufacture using modern low temperature separation techniques was attempted by Schuftan at the instance of the British Oxygen Company. Apart from difficulties associated with the vast quantities of gas to be handled, the amount of ethylene which can be separated depends on how much coke oven gas occurs, or can easily be collected together, in one place and a limit is set to the size of the ethylene extraction and processing plants which may make them uneconomic. When, however, large quantities of coke oven gas are treated by the Linde Bronn or L'Air Liquide process for separation of hydrogen for ammonia manufacture, a side stream much richer in ethylene (15-30 vol. %) is obtained without appreciable extra cost. This is successfully utilized in various places on the scale of a few thousand tons/year of ethylene either to produce ethylene dichloride (for example by MEKOG in Holland) or for further enrichment in special plant to the very high purity required for polythene manufacture, for example by Ethylene Plastique in France.

Going back 30 or 40 years the early types of cracking plants, used to increase the output of motor spirit at oil refineries, gave by-product gases containing considerable quantities of ethylene at reasonable concentrations. However, the demand for larger outputs of better quality motor spirit led to the use of lower temperatures and higher pressures and today the catalytic cracker and hydroformer bear little resemblance to the old crackers. For a given quantity of feed very much less gas is produced and the ethylene in the gas is much more dilute (nearer 5 than 10% by volume on C_2 and lighter) and therefore more difficult to separate. No refinery using modern techniques, at least in Europe, is of sufficient size to give gases containing enough "existent" ethylene to make its separation worth while. The gases will however contain ethane mixed with ethylene and other light bases; separation and cracking of this ethane and recirculation of unchanged ethane for further cracking, will give an increased yield of ethylene. There is also the possibility of propane cracking. Propane can usually be separated from refinery gases as a 60 : 40 mixture with propylene, but the mixture is not immediately suitable for cracking. The propane can be separated from the propylene by fractionation in a

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column of high fractionating ability, or the propylene may already have been removed by sulphuric acid for the manufacture of isopropyl alcohol, or in the manufacture of polymer gasoline. At least some of the propane is usually required for sale as liquefied gas, but if it is assumed that all is available for cracking for ethylene, a refinery of capacity 3 million tons of crude oil a year could provide:

From ethylene already present in the gases	3,500 tons/year ethylene
From the products of the cracking of ethane	4,500 " " "
From the products of the cracking of propane	12,000 " " "
Total	20,000 " " "

Thus a refinery of this size, by recovering the ethylene existent in its gases together with the ethylene made by cracking all the available ethane and propane, could be made to produce 20,000 tons a year of ethylene which is probably about the minimum economic size of an ethylene enrichment plant. The ethylene concentration in the combined gases going to the gas separation plant will be of the order of 16% by volume, which is acceptable, if not optimum.

In the U.S.A., and especially in Texas, where ethane is available from natural gas, ethylene can readily be made by ethane cracking and this is the basis of the largest ethylene plant in the world, namely, the Gulf Oil Corporation's plant at Port Arthur, designed to produce some 80,000 tons/year of ethylene, with a second plant reported to be under construction.

Of especial interest to countries without natural gas supplies, but not confined to those countries, is the deliberate cracking for ethylene of naphtha, gas oil or light distillate, to give the maximum yield of ethylene on feedstock, a maximum volume percentage of ethylene in the gas and, generally, a maximum ratio of olefinic to saturated hydrocarbons. For this purpose the cracking methods of 30 to 40 years ago have been developed towards higher temperatures, lower partial pressures of oil vapour during cracking and short contact times—in fact in the opposite direction to the cracker operating for motor spirit. Normally a yield of about 13% on oily feedstock is regarded as acceptable but a novel technique developed by the M. W. Kellogg Co. which uses steam to provide the heat for cracking, gives yields of over 20% and gas compositions especially suitable for separation of pure ethylene (up to 40 vol. % of C_2H_4 on C_2 and lighter). The Catarole is another cracking process designed primarily for the production of chemicals, as opposed to motor spirit, but with emphasis on the yield of other chemicals as well as ethylene.

In a country where natural gas is not available, the choice for a large source of ethylene probably lies between light oil cracking, especially for

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ethylene, and the cracking of ethane and/or propane from refinery gases combined with the extraction of ethylene existent in the refinery gases. Given a very large refinery, preferably one in which propylene is removed from the C_3 stream for some purpose which can pay for the cost of doing it, and with a large surplus of propane for which no outlet is available giving a higher credit than as fuel gas, the initial cost of the ethylene is probably less than in a light oil cracking process. The cost of ethylene separation from the more concentrated gases from oil cracking will be less than from refinery gases and oil cracking has the considerable advantage of much greater flexibility. The ethylene supply is not limited as to location and quantity by the refinery, and an oil cracking plant can be built so as to provide ethylene and other products most conveniently for the consumer plants. The technology of gas separation is highly developed and costly and the tendency is towards large units and a highly integrated organization leading to the manufacture of a number of end products from the ethylene and other gaseous intermediates.

Available information shows that by 1957 there will be installed plant capacity in the U.K. to produce rich ethylene (90% and over) up to about 109,000 tons/year, made up as follows:

Deliberate oil cracking for ethylene	82.5 %
Propane cracking and ethylene "existent" in refinery gas	11.0 %
Catarole process	6.5 %

and the utilization will probably be roughly:

Polythene	45 %
Ethyl alcohol	25 %
Tetra-ethyl lead chemicals	12 %
Ethylene glycol	8 %
Various ethylene oxide derivatives	7 %
Styrene	3 %

A recent development of great potential importance to countries which have no natural gas which contains ethane, is the investigation which is going on in several countries toward the production of ethylene in 30-40% volume concentration from oils which are cheaper than the light distillate or gas oil currently mainly employed. The objective is to obtain a high weight yield of ethylene and a rich ethylene gas from crude oil or reduced crude. Such oils pose special problems, not met with when using light oils, in transfer to the reaction zone, introduction of the heat necessary to perform the cracking and disposal of the non-gaseous products. In addition, such heavy oils contain less hydrogen and are therefore chemically less suitable as raw materials than light distillate which contains almost as much hydrogen as does ethylene. Lines of solution of these problems are known but considerable development work is still necessary before reliable equipment capable of being constructed in large units can be built.

Until recently the use of ethylene has been confined to the place of production or its near neighbourhood. With the development of transport of ethylene by pipeline or as a liquid in tank wagons, the use of ethylene can be more flexible, and the tendency is to integrate still further the end uses of ethylene and to go to larger production units supplying more varied requirements over larger areas.

POLYMERIZATION AT HIGH PRESSURES

Polymerization of ethylene can take place under a wide range of conditions. For example, at 300°C. and 100 to 200 atmospheres pressure some polymerization occurs, along with other complex reactions, to give liquid products of molecular weight about 100-500. However, the production of a thermoplastic polymer of chain length of the order of one thousand CH_2 groups was first achieved only when the ethylene was subjected to a pressure of about 1000 atmospheres and 200°C. It is now known that polymerization will take place under such conditions in pure ethylene without any catalyst, but the rate of this thermal reaction is less than one tenth of that which can be achieved with suitable catalysts, and, in general, therefore, catalysts are employed in commercial production of polythene. The conditions under which solid polymers with useful properties can be produced economically may be said to lie between pressures of 1,000-3,000 atmospheres and temperatures of 100°C.-300°C. For practical purposes no appreciable reaction occurs in ethylene at 2,000 atmospheres below 100°C. (except with certain catalysts) and in ethylene at 250°C. below about 500 atmospheres. Nevertheless even under these conditions an uncontrollable reaction will propagate if by some mischance it is initiated. Ethylene is only safe from such propagations inside limiting conditions of which the following are examples:

Pressure . . .	1,000 atm.	400 atm.	200 atm.
Temperature . . .	20°C.	100°C.	210°C.

Operations would not normally be carried on above 300°C. as the polymer then undergoes some degradation even in the absence of oxygen.

Pressures greater than 3,000 atmospheres are not normally used, mainly because it has not yet been thought worth while to face the engineering difficulties involved in working at higher pressures for the sake of an increase in the productivity of the reaction stage of the process, nor for the sake of the change in product properties which can be achieved.

Many different catalysts can be used and are used in practice; those hitherto preferred have depended for their action on the generation of free radicals. Oxygen was first used; in this case oxidation of ethylene leads to the production of a free radical. Organic peroxides such as benzoyl peroxide and di-tertiary butyl peroxide have been employed either in aqueous solution, in an organic solvent, or in solution in the ethylene itself. Azo compounds and metal alkyls are also effective. In general, the choice of catalyst is dictated by the temperature at which

it is wished to carry out the polymerization, and this in turn will depend on the type of product it is intended to make, low reaction temperatures being associated with relative freedom from chain branching.

The polymerization of ethylene is highly exothermic, the heat of reaction being about 800 calories per gram and the removal of this large quantity of heat generated in a high pressure vessel is one of the problems of the process. Artificial cooling can be applied to the reactor, but this introduces peculiar problems owing to the viscous nature of the ethylene-polythene mixture, especially at high pass conversion.

The other dominating problem is to prevent the reaction from running out of control. The reaction velocity is increased by an increase in temperature and, as we have already seen, the reaction is strongly exothermic. Hence the reaction is unstable in that any tendency for the velocity to increase will bring about an acceleration in the rate of reaction until it is explosively violent. In such an event the ethylene decomposes to methane, hydrogen and carbon. A reduction in pressure will decrease the rate of polymerisation as will a decrease in catalyst concentration.

The flowsheet for the process is essentially very simple. Ethylene is usually supplied to the plant as a gas at atmospheric temperature and a moderate pressure and it is compressed first in multi-stage compressors of conventional design. From this point the gas is pumped by compressors of special design to the reaction unit. Catalyst is pumped in separately. The critical temperature of ethylene is 10°C . and the critical density 0.22 gm/cc . At 120 atmospheres and 25°C . the density is 0.35 gm/cc . and as the gas enters the reaction stage of the process its density is about 0.5 gm/cc . The gas is thus a relatively incompressible fluid in the later stages of the process. It will be appreciated at once from these figures that a high pressure process has its advantages as well as its difficulties. Polymerization of pure ethylene takes place in a state which the layman would be disposed to call liquid if he had any means of perceiving it. Thus, although the equipment may be heavy and expensive in relation to its volume, it is not expensive in relation to its productive capacity.

The reaction vessel may be a tube or an autoclave. The details of this apparatus are naturally secret and it is not possible to give any further information here. In one version of the high pressure process ethylene is polymerized in a tube in the presence of water and an organic liquid. In this case polymerization may take place either in solution in the liquid, or be propagated in the gas after initiation at the interface between gas and liquid.

Unconverted ethylene is separated from the molten polymer as it emerges from the reaction stage and is recycled. In certain circumstances the unchanged ethylene may be passed on to another consumer, for example, a glycol plant, instead of being returned to the process for re-compression. The advantage of such a purge, of course, lies in the opportunity it affords of accepting a feed gas which is less pure, and therefore cheaper than would otherwise be needed. This advantage

must be weighed against the inconvenience of harnessing one product to another and the waste of energy which may be entailed in compressing gas to a higher pressure than is strictly necessary for the second process.

From this point on, the treatment of the product is carried on in conventional plastics equipment. The polymer is first extruded by a screw or gear pump into a form, for example, a continuous ribbon, in which it can be solidified by cooling and subsequently cut into granules. Some form of hold-up blending of the granules may then be used to average out short-term variations in the grade (or melt index). The product may undergo further processing in Banburys or screw extruders with the object either of mere homogenization, or of incorporating anti-oxidants, carbon black, and other pigments or additives. The problems of handling a molten viscous polymer are substantially the same in the producing plant as they are in the consumers' equipment and this type of equipment, rather than any chemical or physical limitations, dictates the range of grades which are in commercial use. The synthesis plant is capable of producing a wide range of products, from soft waxes to exceedingly tough polymers, but in practice the range of commercial products is bounded by melt viscosities (measured at 190°C.) of about 300 and 300,000 poises.

World production of polythene has risen rapidly since World War II, first, of course, in the United States of America, and more recently in European countries. Some indication of existing capacity and production plans are given in Chapter 31.

HIGH DENSITY POLYTHENE

During the past two years polythenes with different properties from those of the normal commercial products have been made in the laboratory and on the pilot plant scale, and at the time of writing these new products are about to be produced in commercial quantities. The chief characteristics of the new products are higher softening temperatures, greater stiffness and higher density. These properties are those to be expected from a polymer of ethylene in which the molecular chains are relatively free from branches.

Three types of process will be used to produce these new polymers, distinguished chiefly by the catalyst employed, but different also in the process conditions. The catalysts form three groups:

- (1) free radicals;
- (2) supported catalysts;
- (3) metal alkyls.

It must be stated at the outset that the details of the commercial processes which are being developed are secret, and it is therefore not possible to describe them, but the general outline of them is available for the most part in published patent applications or from other sources, and it is on information of this kind that the following account is drawn; the reader must bear in mind that it is incomplete and may indeed be in some particulars inaccurate.

POLYTHENE

The high pressure process previously described employs free radical catalysts. It has been modified by Imperial Chemical Industries to produce a material of density, softening point and stiffness approximating to that made by polymerization with metal alkyls. The essential details which distinguish this process from the normal high pressure process have not yet been made public.

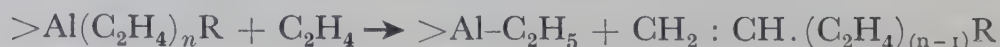
Supported catalysts have been the subject of patent applications, notably by Standard Oil of Indiana and the Phillips Petroleum Company and others. The catalysts mentioned by the Standard Oil Company fall into two groups:

- (1) the metals nickel or cobalt supported on charcoal;
- (2) the oxides of transition metals of Group Va and VIa supported on alumina, titania or zirconia.

The second group is presumed to be used in the projected commercial process, the preferred metal being molybdenum. The metal in the oxide must be in the sub-maximum valency state. In all these cases the polymerization of ethylene takes place at temperatures above 100°C., pressures about 1,000 lb/sq.in., and in the presence of liquid hydrocarbons which serve to dissolve the polymer and maintain the activity of the catalyst. The catalysts are sensitive to air and water, and the process must be operated under dry and reducing conditions. Regeneration of the catalyst is necessary from time to time and may be accomplished by high temperature hydrogenation. The polymer is separated from the solvent by evaporation and is then fractionated by a solvent process to separate the high polymers from liquid or greasy products.

The Phillips Petroleum Company's published patent specifications refer to the active catalyst chromium oxide in the sub-hexavalent state. This is supported on steam activated granular silica-alumina. It is necessary that part of the chromium should be in the hexavalent state, otherwise no polymerization occurs, and the catalyst may be further activated with, for example, strontia. As in the Standard Oil process, polymerization is carried out in a liquid hydrocarbon medium at moderate pressures and temperatures, and similar evaporation and fractionation treatment is involved.

The polymerization of ethylene by the use of certain metal alkyl catalysts has been known for many years. K. Ziegler recently discovered (*Angewandte Chemie*, 64, 323, 1952) that aluminium alkyls were effective and he explained the process as involving first a growth reaction, in which ethylene molecules are inserted stepwise between the aluminium atom and the alkyl group, and subsequently a displacement reaction in which the long chain alkyls are displaced by ethylene leaving an aluminium ethyl derivative



Ziegler later found that by reacting alkyls of metals of Groups II and III with compounds of transition metals in Groups IV to VI insoluble coloured products were formed which could polymerize ethylene. A particularly effective catalyst is obtained by mixing hydrocarbon solutions of titanium tetrachloride and aluminium triethyl. In the absence of oxygen and water, which destroy the catalyst, ethylene is polymerized rapidly at atmospheric pressure, the process starting spontaneously from room temperature. Reaction temperatures rather above 50°C. are preferred.

The first products obtained in this way were of very high molecular weight, and impossible to fabricate by normal techniques. Polymers of molecular weight low enough for processing in normal plastics fabricating machinery have been made by an appropriate choice of the proportions of metal alkyl and transition metal compound used in preparing the catalyst.

The polymerization is carried out in a low boiling organic solvent. The polythene appears as an insoluble precipitate. It is then necessary to filter off the product, remove the solvent, and to treat it to remove the catalyst residues. The product must then be melted, cooled and cut into one or other of the usual granular forms.

ACKNOWLEDGMENTS

The account of ethylene manufacture is substantially drawn from a paper "Routes to Ethylene Manufacture" presented by Dr. J. W. Woolcock to the Fourth World Petroleum Congress and is used by permission of Messrs. Carlo Colombo, 74 Campo, Marzio, Rome.

Other works consulted were: *Journal of the Institute of Petroleum* 1948, 34, 292 pp. 237-246 by R. B. Richards; *Encyclopedia of Chemical Technology*, 10, pp. 938-956 by R. B. Richards; *Chemistry & Industry* 1955, pp. 396-403 by E. Hunter.

Relevant patents on the production of high density polythenes include Standard Oil of Indiana, Belg. Pat. 525,025 (28.4.51); Phillips Petroleum, Aust. Pat. Appln. No. 864/54 (8.6.54); Ziegler, Belg. Pat. 504,160 (21.6.50); Ziegler, Belg. Pat. 533,362 (23.12.53).

CHAPTER 3

THE REACTION KINETICS OF ETHYLENE POLYMERIZATION

E. HUNTER

THE steps of molecular change are often more subtle than stoichiometric equations suggest. In the study of reaction kinetics, the effects of changes in pressure, temperature and composition on the speed and course of chemical reactions are examined and the results are used to disclose the basic processes of molecular change and to reveal the factors which govern the finite rates at which these occur. Although general theory cannot be used without specific measurement to prophesy either whether substances will react or, if they do react, what the reaction velocity will be, once a reaction is known to occur, reaction kinetic measurements in the system can lead to a quantitative understanding of how the reaction is influenced by circumstances. Thus, although reaction kinetic studies can scarcely be claimed to lead directly to the discovery of new reactions, they can be claimed to show how a known reaction can best be promoted, or arrested, or transformed.

In industrial chemistry, the particular value of reaction kinetic studies is the guidance they may give towards improved control of processes and products and towards knowledge of how to secure the most valuable quality of product in the most economic manner. Such knowledge is particularly useful in the manufacture of high polymers for applications in which physical properties are the deciding factor. Product properties are often unexpectedly sensitive to minor changes in reaction conditions and the reactions themselves are made the more difficult to operate satisfactorily by the necessity to provide acceptable product at an acceptable production rate and in acceptable reaction conditions, rather than to be satisfied simply to obtain a certain minimum degree of polymerization of the monomer. Polythene manufacture by the high pressure process demonstrates these points. The lateness of the discovery that high polymers could be obtained from ethylene shows that appropriate reaction conditions are not self-evident, and that the reaction is sensitive to conditions, while the use of the product as a thermoplastic which must be capable of fabrication in the fluid state makes it necessary to study the problem of securing not only satisfactory properties in the solid, but also satisfactory properties in the fluid, yet at the same time avoiding reaction conditions which would entail excessive costs of production.

This chapter cannot give an exhaustive, complete explanation of the reaction kinetics of ethylene polymerization. Firstly, there is not space

for a thorough exposition of reaction kinetic theory as it affects polymerization processes; for this the reader must be referred to the text books, for example "The structure of physical chemistry" by C. N. Hinshelwood for the broad principles of reaction kinetics and "The principles of polymer chemistry" by P. J. Flory for more detailed considerations of polymerization reaction kinetics. Secondly, although much experimental work has been published on the low pressure high temperature gas reactions of ethylene, and many accounts of various ways of obtaining polymers from ethylene appear in the claims of the patent literature, the information in these publications is quite insufficient to prove beyond doubt the reaction mechanisms in each of the various ways of obtaining all the polymers of ethylene. Indeed in very few parts of this wide field has the mechanism been proved; in most parts the evidence barely gives cause for preferring one explanatory theory to another. The scope of this chapter is therefore limited to matters which concern the production of solid polymers of ethylene (polythene), and even here the emphasis is mainly on the factors influencing the high pressure high temperature gas reaction which has been the basis of commercial production up to the present time, ever since it was used in the discovery of polythene in England in 1933.

THE POLYMERIZATION OF ETHYLENE

Neither at low nor at high pressures does ethylene alone show any tendency to polymerize at ordinary temperatures. At very high temperatures it pyrolyses, but by reactions which are so varied and complex, at least at ordinary pressures, that in conditions of not too high temperatures a great variety of compounds can be found in the oily products, including substances which may be regarded as low polymers of ethylene:



Neither these substances nor the mixtures in which they occur are solid. To promote a higher degree of polymerization the Le Chatelier principle suggests the use of higher pressures. Although Amagat had measured ethylene isotherms at pressures up to 1,000 atm. before 1900, experiments on chemical gas reactions at high temperatures were usually limited by technique to a few hundred atmospheres until 25-30 years ago. The application of pressure within this range increased the formation of polymeric products, but they were of low molecular weight, liquids, or at best semi-solids, and until recently, as far as is known, no method using ethylene, even with catalysts, in this moderate pressure range had given product of such a high molecular weight as to be tough and flexible. When it was discovered in 1933 that subjecting ethylene containing traces of oxygen to pressures of about 1,400 atm. at temperatures of about 170°C gave a product of very high molecular weight, wholly solid, tough, flexible and crystalline,¹ the product was novel and the reaction system by which it had been prepared was the only effective one then known. Since that time, careful study of the effect of different catalysts and of

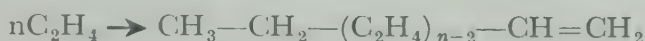
REACTION KINETICS OF ETHYLENE POLYMERIZATION

solvents has broadened the range of conditions in which solid high molecular weight products can be obtained. With certain free radical catalyst systems pressures down to a few hundred atmospheres will give high molecular weight solids, while organo-metallic catalyst systems which until recently only gave solid products if elevated pressures were used² have recently been developed to a stage at which normal pressures are effective.³

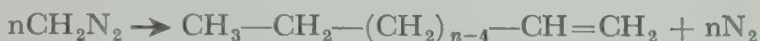
OTHER ROUTES TO HIGH MOLECULAR WEIGHT PARAFFINS

Before passing to the reactions of ethylene, it may be noted that neither in theory nor practice is ethylene the only source of high molecular weight paraffins. Apart from the possibility of obtaining them by fractionating natural products there are the following known syntheses:

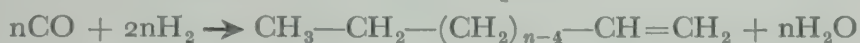
(i) From ethylene¹:



(ii) From diazomethane⁴:



(iii) From hydrogen and carbon monoxide⁵:



All these reactions can be conducted to give high molecular weight solid products, but for the industrial production of thermoplastic products the first is the only reaction employed, presumably because it combines economy with fitness of product. Laboratory studies of the products of the other two reactions have been useful in elucidating the connection between chemical structure and physical properties in high molecular weight paraffins, and it should be remembered that technological interest turns on the products, and will only concern itself with the reaction kinetics of ethylene polymerization as long as manufacture from ethylene shows advantages.

THERMOCHEMISTRY AND EQUILIBRIA IN ETHYLENE REACTIONS

In ethylene at elevated pressures and temperatures decomposition reactions can appear. The sensitivity of compressed ethylene was noted in 1931 by Waterman and Tulleners.⁶ In one of their experiments ethylene was heated safely in an autoclave from 32 atmospheres at room temperature to 350°C and 170 atm., with the formation of only a little liquid. In another experiment, however, which started from 46 atm., the system ran out of control at about 250°C and 130 atm. and reached at least 500°C and 500 atm., with an almost complete conversion to carbon, hydrogen and methane. Since these decomposition reactions are encouraged by high temperatures and are the more violent the higher the pressure, the risk of their appearance has to be guarded against in conducting the polythene reaction in high pressure ethylene. The

polythene reaction is exothermic, and self-heating causes a great risk of decomposition unless special attention is given to methods for removing the heat of reaction, limiting the temperature rise and generally avoiding overheating.

The thermochemistry of some of the possible reactions of ethylene is interesting and shows reasons for the violence of the decomposition reactions. It will be sufficient to consider the heat effects and equilibria in five reactions:

- (1) Polymerization of ethylene to high molecular weight product (polythene)
- (2) Decomposition of ethylene to carbon and hydrogen
- (3) Decomposition of ethylene to carbon and methane
- (4) Decomposition of polythene to carbon and hydrogen
- (5) Decomposition of polythene to carbon and methane.

The thermal effects and equilibria can be calculated from published tables of the properties of hydrocarbons⁷ with the results shown in Table 3.1.

Table 3.1. HEAT EFFECTS AND EQUILIBRIA RELATED TO ETHYLENE AND POLYTHENE

Reaction	K.Cal./mole C ₂ H ₄			
	Heat of reaction (- ΔH)		Free energy change ΔF°	
	500°K 227°C	1,500°K 1,227°C	500°K 227°C	1,500°K 1,227°C
$\text{C}_2\text{H}_4_{\text{gas}} \rightleftharpoons \frac{1}{n} (\text{C}_2\text{H}_4)_n_{\text{polymer gas}}$	22.15	20.17	-5.481	+26.71
$\text{C}_2\text{H}_4_{\text{gas}} \rightleftharpoons 2\text{C}_{\text{solid, graphite}} + 2\text{H}_{2\text{gas}}$	11.14	8.61	-19.245	-37.92
$\text{C}_2\text{H}_4_{\text{gas}} \rightleftharpoons \text{C}_{\text{solid, graphite}} + \text{CH}_{4\text{gas}}$	30.44	30.67	-27.086	-20.13
$\frac{1}{n} (\text{C}_2\text{H}_4)_n_{\text{polymer gas}} \rightleftharpoons 2\text{C}_{\text{solid, graphite}} + 2\text{H}_{2\text{gas}}$	-11.01	-11.56	-13.764	-64.63
$\frac{1}{n} (\text{C}_2\text{H}_4)_n_{\text{polymer gas}} \rightleftharpoons \text{C}_{\text{solid, graphite}} + \text{CH}_{4\text{gas}}$	8.29	10.50	-21.605	-46.84

The first column lists the reactions under consideration, the second and third columns the heat evolved when the reaction proceeds from left to right at the two temperatures 227°C and 1,227°C. The fourth and fifth columns give the free energy changes, again for the reactions proceeding from left to right at 227°C and 1,227°C. When this free energy change is negative, the equilibrium is in favour of the right-hand side of the equation, and, conversely, when it is positive the left-hand side is favoured. The data given apply to gases at atmospheric pressure, but

they can be used at least qualitatively for systems involving liquid polythene and high pressures.

We first note that the polymerization of ethylene is very exothermic, so much so that the heat of reaction for a 25% conversion is sufficient to raise the temperature by more than 300°C at constant pressure. The increase in temperature would be much greater under the constraint of constant volume rather than constant pressure. In closed vessels, as in closed systems in which the change is occurring quickly, conditions approximate to those of constant volume.

Next it is seen that the equilibrium at ordinary pressures—let alone at high pressures—favours the polymer at 227°C, but that at 1,227°C, the reverse or depolymerization reaction is strongly favoured. The decomposition reactions of ethylene to carbon and hydrogen and to carbon and methane, however, are also exothermic—the former less so and the latter more so than the polymerization, and at equilibrium the products of both decomposition reactions are much more favoured than the products of the polymerization reaction, both at 227°C and at 1,227°C.

The polymer also is thermodynamically unstable with respect to carbon and methane by an exothermic reaction and to carbon and hydrogen by an endothermic reaction.

It must be emphasized that thermodynamic instability does not imply that there will be spontaneous reaction at an observable rate from the less to the more stable state. Most hydrocarbons are thermodynamically unstable, yet stable in the every-day sense that in ordinary conditions no decomposition can be detected. Thus, although Table 3.1 shows that if equilibrium could be attained, ethylene and polythene could not persist in significant amounts and their decomposition products would preponderate; it cannot tell whether decomposition will be rapid or imperceptibly slow. Reaction rate will depend on the factors which promote chemical re-arrangement. One of the most potent of these is elevated temperature; the breakdown of hydrocarbons proceeds rapidly at high temperatures. This knowledge, and the data of the table, make it understandable that, in ethylene polymerization, such is the exothermicity of the system that unless great care is taken to avoid an uncontrolled temperature rise there is serious risk of reaching temperatures which will induce the hydrocarbon decomposition reactions, and that these, being themselves exothermic, once induced, will accelerate both because of temperature rise and by the branched chain reactions of the pyrolysis. The data of Table 3.1 also explain the observation that carbon, hydrogen and methane are all found after a decomposition reaction for it seems reasonable to conclude that the more sudden and violent the decomposition, the more will hydrogen preponderate amongst the decomposition products and that milder cases will produce methane rather than hydrogen.

The polymerization reaction is thus seen to be simply one of a number of possible reactions; it is not even the reaction which leads to the most

stable equilibrium. In addition to the difficulties of getting it to occur at all, we must be prepared for difficulties in conducting it smoothly without the intervention of undesired reactions.

GENERAL POINTS IN REACTION KINETIC THEORY

It is a general conclusion of reaction kinetic theory that although molecules must approach each other closely before reaction can occur collision alone is not a sufficient condition: in nearly all cases only a fraction of the collisions result in immediate reaction. To overcome the barrier between the unstable state of the reactant molecules and the more stable state of the product molecules, the encounter must presumably be of a special and rather unusual type. It is necessary that the molecules should bring to the encounter more than a certain minimum of energy known as the activation energy, but it also seems to be necessary for the location of this energy and for the orientation and spatial arrangements of the molecule to be favourable. The obvious way of increasing collision rate to hasten reaction is to increase the concentrations of reactant molecules. The simplest way of increasing the fraction of these encounters involving more than a certain energy is to raise the temperature, for the distribution of energy amongst molecules is such that the small proportion which have energy much in excess of the average is extremely sensitive to and rises rapidly with temperature.

There are certain complicating factors, e.g. the location of energy within molecules fluctuates with time, and in certain types of exothermic reaction the proportion of molecules with high energies may be augmented by product molecules still bearing heat of reaction, but in general, chemical reactions can be expected to show a strong temperature dependence, and one which is stronger the higher the activation energy. The amount of the activation energy, however, varies from reaction to reaction and indeed depends on the precise nature of the reaction steps employed. Thus the same overall reaction may be found to show different rates and activation energies according to whether catalysis is or is not employed, for in some systems catalysts greatly lower the necessary activation energy. The fraction of molecules which in thermal equilibrium possess an energy more than E cal. per gm. mol. in two degrees of freedom of translation is the exponential of $(-E/RT)$ where R is the gas constant and T the absolute temperature, and this is sensitive to the values of the activation energy and temperature. The huge influence of temperature and of the magnitude of E is shown by Table 3.2, which gives the fraction of molecules with energy more than E at temperature T .

Activation energies of say 20,000 cal/mol are not uncommon and the figures show that a temperature change of one or two hundred degrees may, by its effect on the distribution of thermal energy, alter a reaction a million-fold. Yet the figures also show that a reduction in activation energy from a high to a low value can be even more powerful. This confirms the experience that catalysis and environment often produce

REACTION KINETICS OF ETHYLENE POLYMERIZATION

more startling effects in promoting chemical reaction than does increase of temperature.

It is also a general result in reaction kinetics that reactions which stoichiometrically involve a large number of molecules, e.g. $nA \rightarrow A_n$,

Table 3.2. FRACTION OF MOLECULES WITH ENERGY EXCEEDING E CAL./MOL. AT VARIOUS TEMPERATURES

Energy E	Temperature				
	-50°C	0°C	50°C	100°C	150°C
1,000	0.11	0.16	0.21	0.26	0.31
5,000	10^{-5}	10^{-4}	4×10^{-4}	10^{-3}	3×10^{-3}
10,000	10^{-10}	10^{-8}	10^{-7}	10^{-6}	10^{-5}
20,000	10^{-20}	10^{-16}	10^{-13}	10^{-12}	10^{-10}
40,000	10^{-39}	10^{-32}	10^{-27}	10^{-23}	10^{-20}
80,000	10^{-78}	10^{-64}	10^{-54}	10^{-46}	10^{-41}

Energy E	Temperature				
	200°C	250°C	300°C	350°C	400°C
1,000	0.35	0.39	0.42	0.45	0.48
5,000	5×10^{-3}	8×10^{-3}	10^{-2}	2×10^{-2}	2.4×10^{-2}
10,000	3×10^{-5}	7×10^{-5}	2×10^{-4}	3×10^{-4}	6×10^{-4}
20,000	10^{-9}	10^{-8}	3×10^{-8}	10^{-7}	4×10^{-7}
40,000	10^{-18}	10^{-17}	10^{-15}	10^{-14}	10^{-13}
80,000	10^{-37}	10^{-33}	10^{-30}	10^{-28}	10^{-26}

where n is large, proceed by steps each involving very few molecules, usually two and rarely three. A high polymer molecule contains thousands of monomer molecules and we must expect to find that it results not from one single encounter of a horde of monomer molecules but as the result of thousands of repetitions of a step in which a monomer molecule is added to a partly grown molecule. Attention must be centred on the conditions which make possible and promote this vital step.

HIGH POLYMERS FROM VINYL COMPOUNDS BY FREE RADICAL INITIATION AND GROWTH

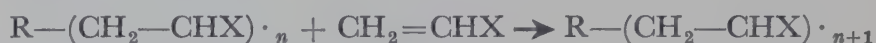
Although all high polymers depend on some such step, there is a wide variation in the chemical changes involved. In nylon for example the step is a condensation between carboxylic and amine groups at the ends of molecules, with the linking up of chains (which may already be long) and the elimination of water. In the case of ethylene, polymer alone is the main product and there is no question of an elimination reaction. The step must presumably be simply a repeated addition of the C_2H_4 molecule. In the product its ultimate form is as the group $-\text{CH}_2-\text{CH}_2-$ but there remains the question of the structure of the

body to which it adds and which thereby becomes simply a higher member of the same homologous series.

The last question can be answered from the behaviour of vinyl compounds. These have the general formula $\text{CH}_2 = \text{CHX}$, and ethylene might be expected to show some resemblance to them. The class includes vinyl chloride and acetate, methyl methacrylate and styrene and many others which yield high polymers in remarkably similar conditions by reactions which are demonstrably chain reactions, susceptible to catalysis, photo-activation and inhibition. Examples of these reactions have been much studied, not only in solution but also in undiluted liquid and gaseous monomer. There is general agreement that the chain reaction consists of a repetitive step which is an addition reaction of a free radical and a monomer molecule to give a larger free radical, e.g.



and in the general case

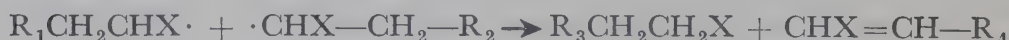


The smaller alkyl radicals have been prepared and studied and shown to be very reactive and consequently short-lived. The longer chain radicals can be assumed to be reactive also.

It should be noted that it is essential to provide means which introduce free radicals into the system to initiate these chains, and that the process of addition of monomer to free radical is much easier than the addition of monomer to pure monomer, which seems to be difficult. There are unavoidable processes which destroy radicals and so reduce the number of growing chains. Apart from the fact that radicals are chemically very reactive and easily removed by many substances which might be present as impurities, there are two main processes known to end radical growth, although their relative importance may depend on reaction conditions. The first of these is the mutual destruction of radicals to give either one or two "dead" product molecules. This is illustrated by the equations:



or

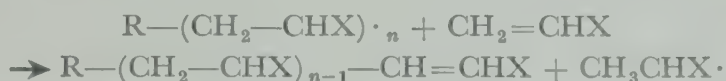


Where R_3 and R_4 may differ from R_1 and R_2 but together have the same number of carbon atoms.

If the radicals only appear from the growth of initiating radicals there is here a simple ratio between the number of chains started by radicals and the number of ultimate product molecules.

The other process is chain transfer. Here the centre of growth of the radical shifts to a new position either within the same molecule or to another one, as the result of an internal re-arrangement in the one case and in the other case as the result of a reaction between growing radical and a molecule of monomer, solvent or product. A shift of the position

of the active centre by re-arrangement affects the structure of the ultimate product molecule, but does not stop the radical growth. The other reactions, however, can lead to the formation of a "dead" polymer molecule from the growing radical and the simultaneous appearance of a different free radical capable once again of growth. Many variations are imaginable, but a hypothetical reaction with monomer will serve to illustrate the effect of transfer:



In this process there is no fixed relationship between the number of original initiating radicals and the number of "dead" product molecules ultimately formed.

Obviously, no large radical is formed except by the growth of smaller ones, each of which has been exposed to the risk of termination reactions at every stage of its growth. At each stage the chance of growth rather than termination is less than unity and the chance of an initiated chain growing to a radical containing a large number n of monomer units is the n th power of its fractional chance of passing a single step. For long chain radicals the chance of termination must be kept very small compared to that of growth—a 50-50 chance of growth to 1,000 units requires odds on survival at each step to be more than 1,400 to 1.

Radicals which are effective in chain initiation are readily provided, commonly by the decomposition in the system of some suitable substance added for the purpose, or formed in the medium by the action of radiation. The most familiar source is an organic peroxide which decomposes at the temperature employed for the polymerisation.



Such substances have been called "catalysts." They are not so in the original sense of this word, but since one free radical from such a substance may stimulate the reaction of thousands of monomer molecules there is the resemblance to true catalysts that a small quantity may produce large effects.

The influence of reaction conditions on the overall rate of reaction (i.e. the rate of disappearance of monomer) and on the average molecular weight of the product depends very much on the factors which terminate the growth and so affect the average life of the radicals. The overall rate can be regarded either as the product of the standing concentration of radicals and the rate of growth of the average individual radical, or as the product of the rate of appearance of new radicals of any origin and the number of monomer molecules the average radical succeeds in uniting with before its termination. Increasing the catalyst concentration will increase the rate of initiation of chains and so can be expected to increase the standing concentration of radicals and hence to increase overall rate. But this result will be modified if termination is chiefly by mutual destruction of radicals, for the greater the standing concentration

of radicals the greater is the risk of termination for a single radical and so the shorter is the life of the average radical. More radicals will grow, but to a shorter average length than before. In the simplest case of such a mechanism, rate would be expected to vary directly as, and average molecular weight of product inversely as, the square root of the catalyst concentration and both rate and molecular weight would vary linearly with monomer concentration through the effect of this on the rate of the individual growth steps. Approximations to this behaviour are found, especially when the temperatures employed are not high, but there are usually signs that chain transfer is occurring.

When chain transfer rather than mutual termination is preponderant, the life of the individual radical will not be shortened by increasing the standing concentration of radicals and increase of catalyst concentration would be expected to increase overall rate with little effect on molecular weight. Molecular weight, however, which depends on the average length reached by the radical, is very dependent on the causes and circumstances of the chain transfer. Chain transfer reduces molecular weight but the overall rate may be sustained in spite of it, since the act of transfer does not reduce the number of growing radicals. Many more product molecules are formed than correspond to the number of chains initiated by catalyst molecules; the balance come from chains initiated by the radicals formed in the chain transfer process. The extent to which average molecular weight is reduced, without major effect on the overall rate varies greatly with the transfer agent; the chemical interactions between the growing radical and molecules of the chain transfer agent are apparently highly specific.

It will be appreciated that since catalyst and catalyst concentration, solvent and monomer concentration, and temperature may all influence rate or molecular weight, or both, there is usually wide scope for the manipulation of the reaction.

ETHYLENE POLYMERIZATION AS FREE RADICAL GROWTH

The behaviour of ethylene in free radical polymerization proves to be sufficiently akin to that of the familiar vinyl compounds for the above account of the general reaction mechanism to serve for the ethylene case. Although there is no evidence of any fundamental difference in reaction mechanism, there is however one striking quantitative difference in behaviour. The vinyl compounds which readily give high polymers by free radical initiation do so over a wide range of monomer concentration. Methyl methacrylate can be polymerized to a solid not only in the undiluted liquid state but also, by photosensitized catalysis, in the vapour phase at less than atmospheric pressure. This range of concentration must correspond to more than a ten thousand-fold change in the rate of collision of a growing radical with monomer molecules. In such cases the growing radical must be considered to be comparatively stable, neither prone to internal re-arrangement nor demanding a high activation energy of growth.

REACTION KINETICS OF ETHYLENE POLYMERIZATION

Ethylene is found to react additively with free radicals but at low pressures the product is not of high molecular weight. High concentrations of ethylene seem to be essential to obtain high molecular weight from chains initiated by free radicals. In a low pressure study of ethylene polymerization using free radicals obtained by the U.V. photolysis of acetaldehyde, Danby and Hinshelwood⁸ in 1941 found that the reason for the absence of high polymers was not that ethylene fails to react additively with free radicals at low pressures, but that in reacting it forms radicals which very readily undergo changes which terminate their growth. This work emphasized that production of high polymer depends on the chance of a radical's growth being vastly greater than its chance of undergoing other reactions, and suggested that in ethylene the chance of radical growth is unusually dependent on the time interval between collisions with monomer molecules. This accords with the observation that if a high ethylene concentration is provided by the use of high pressures, free radical initiation leads to high molecular weight products.

It is difficult to make a quantitative reaction kinetic study of the high pressure reaction. Because of the limitations of technique set by the

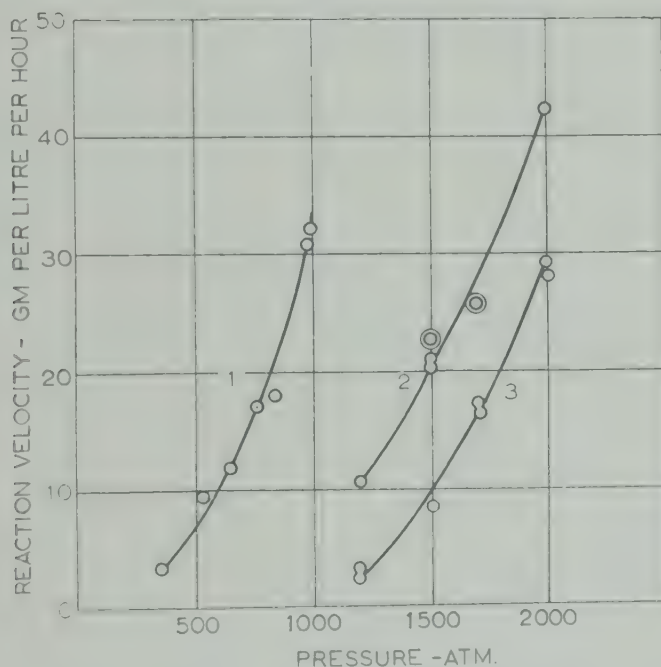


Fig. 3.1. Effect of pressure on reaction velocity in laboratory experiments:

1. With di-tertiary butyl peroxide at 140°C
2. With acetoxime at 200°C
3. Virtually catalyst-free gas at 230°C

high pressures and because of the intense heat release, full use cannot be made of two of the most powerful methods of reaction kinetics, measurement of composition change during reaction and variation of the reaction velocity over an enormously wide range. It is possible to make some measurements, however, which help towards an understanding of the

reaction. Fig. 3.1 shows the results of some measurements made at Northwich by Laird, Morrell and others on the gaseous polymerization. These experiments were carried out in small batch vessels at constant pressure. By using a Cailletet press and a very sensitive pressure gauge, e.g. a manganin resistance gauge, the volume change during reaction at constant temperature and pressure can be measured. It depends on the density difference between ethylene and polythene and is readily calibrated against the mass of product found after the experiment is completed. The first curve of Fig. 3.1 is with di-tertiary butyl peroxide as catalyst at 140°C, the second with acetoxime at 200°C, and the third is for virtually catalyst-free gas at 230°C. These curves show the main effects of pressure, temperature and catalyst concentration on reaction rate. Increase in any of the three causes a big increase in rate but the extreme dependency of rate on pressure is especially to be noted.

A given reaction rate can be obtained with an infinite number of combinations of these three reaction conditions, for an increase in one can be employed to offset a reduction in another. Use is made of this principle in control in manufacture. But the average molecular weight of the product does not depend on reaction conditions in precisely the same way as the rate does. It is increased at constant temperature and catalyst concentration by increase of pressure, but increase of temperature and increase of catalyst concentration, especially the former, both cause some reduction of average molecular weight. The existence of the three variables and the difference in the dependencies of rate and chain length upon them provides the possibility not only of obtaining either high or low chain length product at the same rate by suitable choice of a combination of reaction conditions but also of using different combinations of conditions to give product of given chain length at a given rate. The value of this flexibility will be referred to later.

THE SIGNIFICANCE OF PRESSURE IN THE REACTION

The great sensitivity of rate to ethylene pressure directs attention to the relationships of pressure, temperature and volume in ethylene. Fig. 3.2 shows how the density depends on pressure and temperature. The critical point of ethylene is at 10°C and about 50 atm., where its density is about 0.22 gm/cc. It is seen that considerably higher densities obtain at the high pressures used in polymerization, for example in the experiments whose results appear in Fig. 3.1. It is also seen that at these high densities the gas becomes relatively incompressible compared to an ideal gas (incidentally showing that pressure cannot be used as a linear measure of concentration as it is in low pressure reaction kinetics).

The maximum dimension of the ethylene molecule is thought to be about 5.5 Ångstrom units and from this it can be calculated that the maximum density of loosely packed unoriented molecules is no more than 0.28 gm/cc. It follows that at the densities prevailing in the high pressure synthesis (the ethylene densities of the experimental points in

Fig. 3.1 all exceed 0.3 gm/cc, e.g. at 200°C and 1,500 atm. the density is about 0.46 gm/cc.) most of the molecular collisions, rather than only the most severe, must involve distortions or orientations. It is not a simple matter to decide whether the effect of high pressure in promoting radical growth is due simply to the rapid rise in collision number which must occur as the molecules become closely packed and the free volume rapidly diminishes or whether it arises from molecular orientation or distortion associated with high pressures.

In low pressure gases, collision number can be calculated with fair approximation and the results are helpful in considering the relative

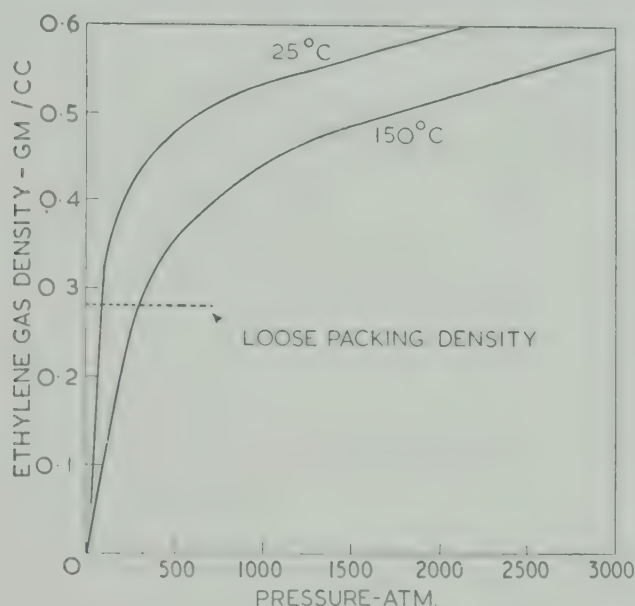


Fig. 3.2. Density of ethylene at high pressures, at 25°C and 150°C

importance of the various factors influencing the reaction kinetics. Such calculations become more difficult and less trustworthy at higher pressures and densities, and when the average distance between molecular centres becomes little more than the molecular diameters, the results are very uncertain. The thermodynamic properties of ethylene at high pressure, however, are accurately known⁹ from Michels' measurements and it is profitable to consider whether this knowledge can help towards an understanding of the reaction kinetics of ethylene polymerization.

In the first place an alternative formulation of the factors influencing reaction velocity can be examined. This uses thermodynamic concepts instead of the primarily kinetic approach so far used in this account. This transition state theory is based on the idea that there is a transition complex (in some respects intermediate between reactants and products but peculiar in its state of energy and spatial arrangement) which is in true thermodynamic equilibrium with the reactants. It is transformed to the final product at a frequency depending only on temperature, so that the rate of appearance of product depends chiefly on the concentration

of the transition complex. If this idea is applied to the growth step of long chain radicals we write



The equilibrium between reactants and transition complex gives

$$[R\cdot CH_2\cdot CH\cdot_2^*] = k[R\cdot][C_2H_4]$$

where k is the equilibrium constant and the square brackets denote the

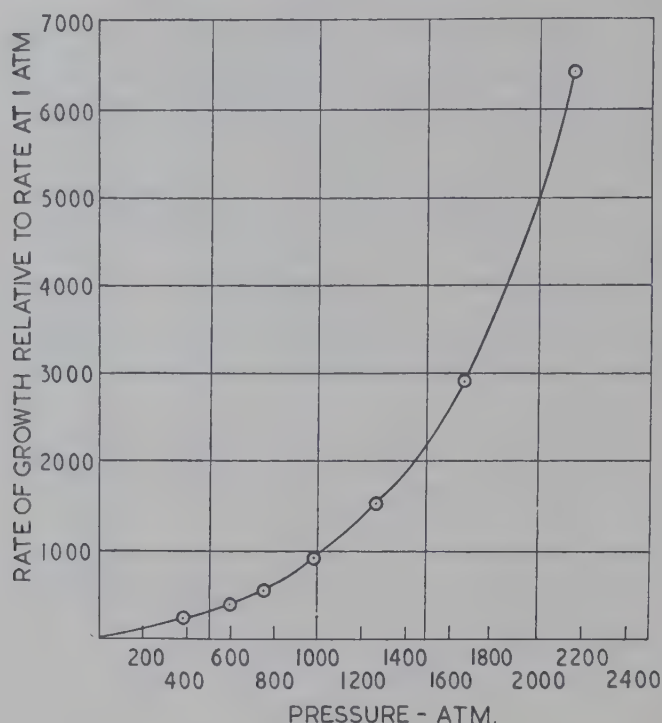


Fig. 3.3. Calculated effect of ethylene pressure on rate of free radical growth

thermodynamic activities which replace concentrations in the rigid treatment of mass action and chemical equilibria.

The activity of the transition complex is seen to increase with the activity of the radical and of the ethylene from which it is formed. Because activity is an exponential function of free energy change and because the free energy changes in ethylene become very great as high pressures are reached, the activity of ethylene rises remarkably steeply at high pressures. This is shown in Fig. 3.3 where values of the activity relative to that at atmospheric pressure are shown for pressures up to 2,200 atm. at 150°C. A corresponding increase in the activity of the transition complex and hence in the rate of the chain growth reaction might be expected. There is indeed a strong resemblance between the curve of Fig. 3.3 and the experimental results shown in Fig. 3.1. It must be remembered that the experiments concern overall rate, not merely the rate of chain growth, and if pressure promotes the initiation of chains, the increase in overall rate to be expected will be greater than that indicated by Fig. 3.3. The differences in detail between the experimental curves and the ethylene activity curve can be attributed not only to this but

also to a smaller extent to the probability that the activity coefficients of the transition state radical and of the growing radical are not constants which are independent of ethylene pressure.

Although these calculations give some theoretical support for the observed effect of pressure on rate, they give no detailed explanation of mechanism, for abnormal activity includes and does not distinguish between abnormal concentration effects (collision number) and abnormal orientations and energy changes. It is however possible to calculate the energy changes caused by compression. The basis of these calculations has been given by A. Michels and S. R. de Groot.¹⁰ Fig. 3.4 shows the results of such calculations for 150° with changes of the internal energy ΔU and the contributory terms of kinetic and potential energy changes ΔK and ΔV_e shown against the average distance between molecular centres. The changes are small until the molecules are closely packed, but thereafter they become as large as the activation energies of

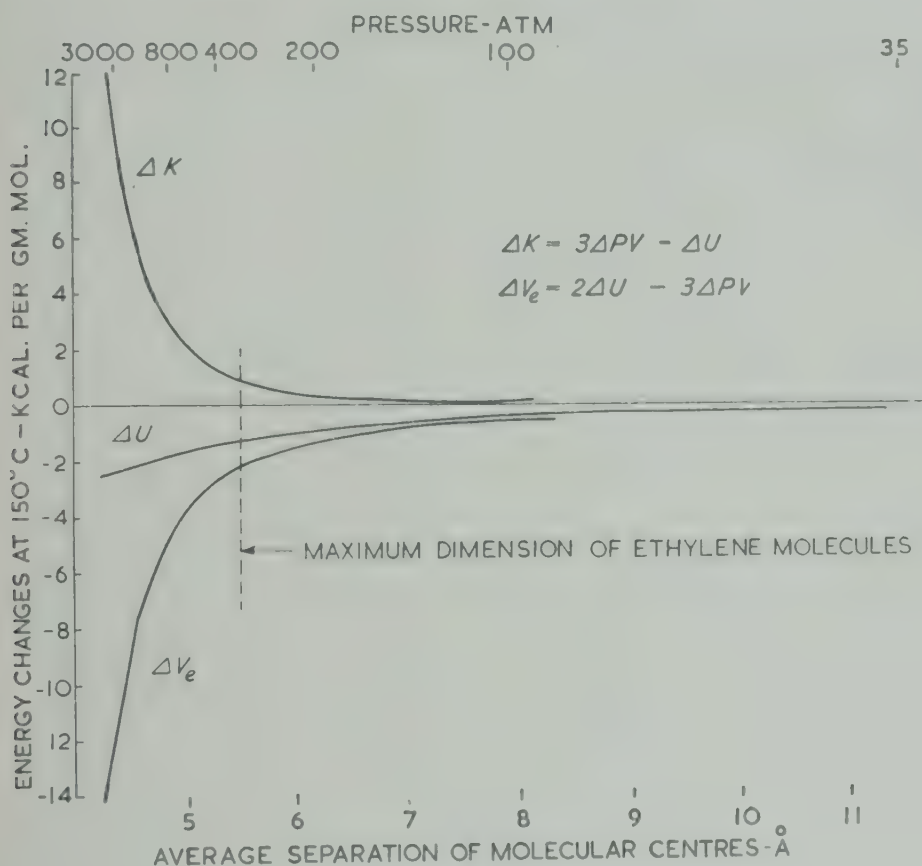


Fig. 3.4. Energy changes in ethylene at 150°C on compression

some chemical reactions and might seem to prove that the high pressure has brought about a great change of chemical reactivity. However, it must be remembered that the type of behaviour shown in Fig. 3.4 is not peculiar to ethylene. Similar effects will be found with any substance whose molecules have a finite size and exert forces on each other. In propylene, for example, the energy changes are just as great as in ethylene,

over much the same range, yet high polymers are not obtainable from propylene by free radical initiation at low or at high pressures. The great changes in collision number and energy which occur in ethylene at high pressures must play a very important part in the reaction but by accelerating its rate rather than by causing it—after all we return to the fact that without catalyst at ordinary temperatures the high pressure gas does not react. The likeliest explanation seems to be that while on the one hand vinyl compounds such as styrene and methacrylate can give large free radicals which are fairly stable against deactivation and internal rearrangement, and on the other hand propylene reacts with initiating radicals to give radicals which too readily undergo a destructive rearrangement, ethylene occupies an intermediate position giving radicals whose lifetime to deactivation or re-arrangement is shorter than the time lapse between favourably oriented collisions at low pressures, but longer than the time lapse between these collisions at high pressures.

Although with free radical polymerization of ethylene it seems necessary, for high polymers, to provide more than a certain minimum collision frequency between the radical and the ethylene molecules, there are reasons for believing that if the collision frequency were indefinitely increased, by the use of higher and higher pressures, there would not be a corresponding increase in chain length of product. The heat of polymerization is 23 K. cal/gm mole ethylene and the equivalent of this will be released on each occasion when the growing radical unites with an ethylene molecule. This large energy associated with the radical immediately after its growth will be more than sufficient to provide the activation energy needed for further growth. When collision frequency is low there will be some risk that this excess energy will be lost from the radical by unprofitable collisions along its length before there is a favourable collision with the active "head," and also a risk that if the energy is not lost yet the time lapse before a growth is long, internal chemical re-arrangements will occur. When collision frequency is high, however, the risk will be rather that the successive additions of ethylene molecules to the chain, each releasing 23 K. cal/gm mole at the growing "head," will give the radical such a great excess of energy, that disruptive reactions will be encouraged. The energy of the carbon-carbon bond for example is roughly 60–65 K. cals and the activation energy of a variety of breakdown reactions with ethylene, which may include chain transfer, will readily be reached if the chain growth is too fast. Increase in the rate of these reactions will tend to increase the rate of disappearance of ethylene but at the same time will prevent the attainment of very high molecular weights and will promote chain transfer, in extreme cases perhaps with the intervention of decomposition reactions as kinetically branched chain explosions. On this view it will be necessary to keep the growing radical between two limiting energy levels, the lower one the activation energy for chain growth (coupled with a collision frequency high enough to secure growth rather than internal re-arrangement) and the upper one that of the activation energy of chain transfer or of pyrolysis. Certainly

REACTION KINETICS OF ETHYLENE POLYMERIZATION

in practice the range over which pressure can usefully be varied with all other reaction conditions constant is limited, through the tendency for the reaction on the one hand to become uncontrollably fast as the pressure rises, and on the other to cease abruptly as the pressure falls.

This theory also suggests that the type of reaction governed by mutual chain termination will be associated with moderate reaction velocities especially at low temperatures, and that in conditions of high rates induced by high pressures with high temperatures, the reaction will show more complicated features of termination, possibly a number of competing processes, with chain transfer a prominent feature. Experimental support for this is that the simplest and most nearly linear chain product is made at low temperatures while at high temperatures the product structure becomes more complex and that with high temperature catalysis with oxygen the number of molecules produced very greatly exceeds the number of oxygen molecules consumed.

TEMPERATURE AND CHAIN INITIATION AND GROWTH

The density of ethylene increases not only with pressure but also with falling temperature. As is shown in Fig. 3.2 a density of 0.4 g/cc. which requires 700 atm. at 150°C can be obtained with 200 atm. at 25°C. It might be asked whether, if high concentrations of ethylene are so effective in the free radical polymerization, the necessary conditions of high concentration for the high polymer reaction can be obtained at much lower pressures by working at much lower temperatures, perhaps even in the liquefied gas. To some extent this can be done but everything depends on finding a low temperature source of the initiating free radicals. There is a wide variety of free radical-producing substances with different degrees of temperature stability which can be chosen and from these it is simple to cover the temperature range from 200–250°C down to the region of 50°C. Here experiment shows that pressures of a few hundred atmospheres are still necessary. At room temperature it is now possible to generate free radicals by exposing the compressed ethylene to an intense source of γ -rays, which forms them by attack on the ethylene. When this is done a pressure of some hundreds of atmospheres is again found necessary to give any signs of high polymeric reactions. At low temperatures these reactions are slower than might have been expected from the ethylene densities employed. This and the fact that with γ -radiation (which can be employed over a wider temperature range than other catalysts) the reaction shows a considerable increase in velocity as high temperatures are reached are probably signs that the activation energy of growth is not insignificant and that in the normal synthesis methods which operate at high temperatures chain transfer occurs to a significant extent.

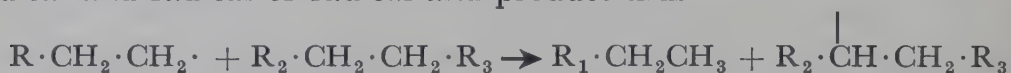
CHAIN BRANCHING IN POLYTHENE

In general, different reactions have different activation energies and consequently different temperature coefficients. Thus at high temperatures reactions with high activation energies can become noticeable

which are not apparent at low temperatures. It was originally thought that polythene consisted simply of linear paraffinic chains, but it was then found that in the normal commercial product there were many more methyl groups than would correspond simply to two end groups for each molecule known to be present.¹¹ In substances known on the average to have more than 1,000 carbon-carbon bonds per molecule, between one and three methyl groups are usually found for each 100 $\text{—CH}_2\text{—}$ groups. This is evidence that the molecules have branches, of unknown length. By chemical standards this amount of branching might not seem high, but the flow properties of long chain substances in the molten state and their mechanical properties in the solid state seem to be sensitive to such amounts and the matter has been given much attention. It must first be said, as an experimental observation, that the simplest and most effective way of changing the amount of branching is to alter the reaction temperature for it rises and falls as the reaction temperature rises and falls. But in considering the effects of branching on product properties a great distinction is drawn between short branches and very long branches, both of which may be present. Crystallinity, which influences mechanical properties, is affected by branching, but there is no obvious reason why long branches should disturb this more than short branches. In the fluid, however, the flow behaviour which is important in fabrication would be expected to be quite different for molecules with long branches than for those with short. The theory has been advanced that the main origin of short branches is an intra molecular hydrogen transfer occurring via a transient cyclization to a 5- or 6-membered ring.¹² The overall effect is a movement of the active centre to a point down the chain:



The long chain branching is attributed to transfer reactions between radical and radical or radical and product thus



With this mechanism, which is bimolecular, one consequence would be that with other things equal, high concentrations of product, i.e. high conversions, would tend to give more long branches on chains. It is difficult to prove this and similar points beyond doubt because of difficulties of technique including the absence of simple direct methods for measuring the lengths of chains. The subject is still under review but it may be pointed out that as with other bimolecular reactions the velocity will depend not only on concentrations but, through the reaction velocity constant, on temperature and increase in temperature can be expected to increase the chance of this type of branching. It may be possible for conditions of high conversions but low temperature to show less long chain branching than conditions of low conversion and high temperature.

In theory the connection between the reaction mechanism of a polymerization and the molecular weight distribution of the products of

reaction might be used, by employing studies of molecular distribution, to answer questions of reaction mechanism. In practice this has not yet been sufficiently elaborated to be of much use. First, fractionation and characterization cannot be done with adequate precision; secondly, the possibility of concurrent reactions shown to exist by the presence of branching confuses the issue and finally it is difficult to comply with the basis of the idea which requires samples to be formed in absolutely constant, known, reaction conditions and not over a range of conditions which would inevitably broaden the distribution.

Although the branching has profound effects on physical properties, it is not extensive in chemical terms and the overall effect on ethylene polymerization reaction velocity does not seem to be important.

The variety of initiators which could be employed for free radical polymerization of ethylene was early appreciated, but the mode of action was not immediately understood, for it was at first thought that the differences in the products they yielded were due to specific effects of the initiators. This is not so, at least with moderate concentrations of catalyst. At high concentrations some catalysts, e.g. benzoyl peroxide, oxygen, etc., make a direct oxidative chemical attack on the product. Different catalysts produce free radicals at different rates at any particular temperature, so that for a reasonable rate of reaction it is usually necessary to alter the operating temperature if the catalyst is changed. In the absence of added catalyst there is a thermal reaction at sufficiently high temperatures (cf. Fig. 3.1) which is presumably initiated by radicals generated at these temperatures from ethylene. It has been said that branching changes with temperature, and in the free radical polymerization of gaseous ethylene, differences of product type, by which is understood differences between products of roughly similar molecular weight, can usually be attributed directly and solely to the different synthesis temperatures which have been employed in making them. This principle may possibly extend to ethylene polymerization by ionic catalysis, for this method, usually operated at normal or only moderately elevated temperatures, apparently gives almost wholly linear products. The high molecular weight paraffins from diazomethane are also almost wholly free from branching.

One important reason for the fact that commercial manufacture has employed high temperatures and pressures has been that a branched chain product rather than a purely linear one has the commercially attractive combination of flexibility, freedom from brittleness and good extrudability. This has required a substance of not too great a crystallinity and complete crystallinity is apparently avoidable by the introduction of the kinds of branching which appear in the high temperature synthesis. Still less crystalline and more rubbery products can be made by the use of co-polymerization with monomers containing large groups which will interfere with crystallization.¹³ The ability to use different combinations of temperature, pressure, catalyst concentration and gas composition, makes it possible to vary product structure and properties

without serious change of chain length. This flexibility of the high pressure free radical polymerization has not yet been fully exploited.

THE EFFECT OF ETHYLENE COMPOSITION

In the free radical polymerization the addition of quite low concentrations of second components usually has very marked effects. If a substance is merely inert, with no direct chemical effect on initiator, growing radical, or product it nevertheless lowers the effective ethylene concentration, and by an amount which may seem surprising until the relative incompressibility of ethylene is remembered. Thus it is seen from Fig. 3.2 that the presence of say 10% of nitrogen will make it necessary at 150°C to use more than 2,000 atm. to obtain the ethylene concentration of the pure gas at 1,500 atm., i.e. an increase of 500 atm. rather than the 150 atm. for an ideal gas mixture. Small amounts of inerts thus tend to reduce reaction rate and molecular weight.

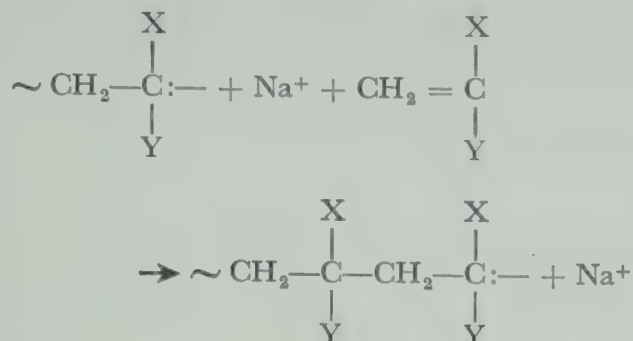
Many impurities have specific effects.¹⁴ Vinyl substances generally interpolymerize with ethylene and affect the properties of the product without necessarily showing major effects on the rate. Acetylene also reacts with the growing radicals but tends to have a deleterious effect on molecular weight and other properties of the product. Some substances, e.g. water and benzene, have singularly little effect, but there is a large class of substances which cause chain transfer. These vary greatly in chemical nature, e.g. hydrogen, cyclohexane and esters. No general description can be given of their effects, indeed it is not always known whether they form single or two-phase systems with ethylene. The observations that while nitrogen or ethane, both inert, reduce rate and molecular weight, yet benzene apparently has little effect on either, is a reminder that the interactions between different molecular species are often not only less predictable but also more remarkable in consequences than the changes in reaction velocity brought about by changes in energy distribution and collision number through changes of temperature and concentration.

Many complicated systems have been examined. Even in the field of free radical polymerization these include systems to which a great variety of second or even third components have been added. These systems have included substances chosen for a number of purposes, e.g. water and other liquids to improve the thermal stability of the system, or to dissolve the product, or to give low molecular weight products by chain transfer. Very little is known of the reaction kinetics of such systems which are made difficult by the unknown phase relationships.

POLYMERIZATION OF ETHYLENE BY IONIC GROWTH

The chain growth of vinyl compounds and ethylene can proceed by other routes than free radical initiation and growth. Alkali metals and their hydrides and some metal alkyls induce an anionic polymerization

of some monomers, e.g. methyl methacrylate is reported to be polymerized by sodium in liquid ammonia. In these systems of polymerization the growth step is symbolized by Flory as



In the polymerization of vinyl compounds these methods have not in the past shown the same generality as the free radical methods. Their efficacy varies greatly from case to case and although with some monomers, e.g. isobutene, ionic polymerization has given high molecular weight products at high reaction rates, with others, and especially with ethylene, rates and molecular weights have tended to be lower. For example, a 1941 patent¹⁵ quotes an example in which a hard brittle polymer of m.p. 106–110°C was obtained from ethylene at about 50–60 atm. and 35–50°C using a benzene solution of lithium butyl with reduced nickel. No improvement of product properties in the direction of increased strength and flexibility, except by the use of high pressures at temperatures high enough to decompose the metal alkyl to give free radicals capable of initiating radical chains, has been claimed until recently. Ziegler³ has recently discovered improved catalytic systems of the organo-metallic type which make possible the production of high molecular weight solids from ethylene at normal pressure. The mechanism here appears to be anionic catalysis rather than free radical growth; some fundamental difference of mechanism seems to be necessary to explain the utterly different dependencies of the two systems on ethylene pressure. Evidently substances exist which in forming carbanionic centres for growth with ethylene do so in a manner which provides a less unstable entity than the free radical of free radical initiated growth yet one which readily reacts additively with ethylene.

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CHAPTER 4

COMPOUNDING

H. A. RIGBY

COMPOUNDING is the term used to describe the processing of polythene with additives so as to produce a uniform and homogeneous product. Ideally, the polythene additives in the individual granules of the compound should be in the state in which they are required in the product which is to be fabricated from the compound. However, if the compound is to be used for a specific subsequent process, it may be adequate to partially compound as a first stage and to complete the compounding in the final process.

The equipment used for compounding depends on the scale of operation and the quality called for in the product. The process of manufacturing a compound can be divided into the stages of blending, compounding and subsequent granulation of the product.

BLENDING

To ensure the manufacture of a product of uniform composition it is often desirable to mix the components thoroughly before the polythene is melted. This is not necessary on a laboratory mill since good mixing can be ensured by repeated removal from the mill and passage through the nip. In a Banbury mixer the components are fed cold and the time elapsing between dropping the ram and the polythene melting is adequate for the production of a satisfactory dry blend. Other types of compounding equipment operate continuously rather than batchwise and it is then necessary either to blend in bulk or to use a number of metered component feed systems. The accurate control of proportionating feed systems for a variety of dry powders and polythene granules presents considerable difficulties and this method of feeding has not yet been widely adopted. The practice of dry tumble blending is common and satisfactory results can generally be obtained by this method. In its simplest form, a drum is approximately half filled with the components, loading first half the polythene, then the additive, then the remainder of the polythene. After sealing, the drum is then rotated end over end at a speed of between 40 and 60 rev/min for about 15 minutes. This method will generally give a satisfactory distribution of a small percentage of dry powders with polythene granules. It is not always satisfactory, however, for blending polythene granules with master batches of additives in polythene unless the virgin polythene and master batch granules are approximately the same shape, size and density. With granules of different sizes segregation can occur. For large scale operation a variety of tumble and ribbon

blenders is available, but probably the most efficient blenders for polythene are those whose outer shell rotates giving a tumble blending action while an internal paddle or ribbon rotates at a higher speed.

COMPOUNDING BY ROLL MILL AND BANBURY

To produce high quality dispersions of pigment, it is essential that the equipment used should be capable of first fusing the polythene, then breaking down any pigment agglomerates by the application of high shear stresses in the melt and then producing a homogeneous melt as a result of effective mixing. When masterbatch techniques are used, the aim is to disperse the pigments effectively in the masterbatch so that when the masterbatch is diluted only efficient mixing is required.

The two roll mill

On a laboratory scale, the small two roll mill is the most convenient equipment to use for compounding. With a polythene of melt flow index 2 the front roll is usually controlled at a temperature of about 130°C and with a back roll temperature of about 90°C, the polythene sheet adheres to the front roll from which it is repeatedly removed, using a doctor knife, and returned to the nip of the mill for an overall time of about 10 minutes. The pigments or the pigment master batch can be added either by prior tumble blending or directly to the mill after the polythene has fused.

Commonly used roll sizes are 6 in. diameter \times 12 in. long and 9 in. diameter \times 18 in. long. The optimum charges for these mills are about 1 lb. and 4 lb. respectively. Typical speeds of operation are 30 rev/min for the smaller and 25 rev/min for the larger. For simple mixing an open nip can be used, but for dispersing pigments a tight nip is most effective.

The Banbury mixer

For large scale compounding the most widely used and versatile equipment is the Banbury mixer (Fig. 4. 1 and Plate 4. 1). This consists of a jacketed chamber whose cross section is in the shape of a figure eight in which two cored specially shaped rotors counter-rotate at slightly differing speeds inducing a kneading action between the rotors and a shearing action between the rotors and chamber. The chamber is closed below by a cored sliding door and above by a compressed air operated ram, also cored, which moves vertically in a hopper down which the polythene is charged to the chamber of the mixer. The Banbury mixer is produced in a range of sizes, of which the 3A is the most generally used for polythene compounding. This size is generally fitted with a 150 h.p. motor which drives the rotors at a speed of about 35 rev/min although higher powered motors can be used to permit rotor speeds of about 35 or 70 rev/min as desired. The optimum charge size for a 3A Banbury is generally about 80 lb. of polythene and additives, but varies a little from machine to machine and has to be determined individually. This is done by

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increasing the charge size until the quantity of material present when the polythene has melted is just sufficient to cause the ram to lift from its bottom position: this ensures that no dead spot occurs in the hopper. Half the polythene is placed in the chamber and this is followed by the additives and then the remainder of the polythene. When the additives are in liquid form it is preferable to add them slowly when the polythene has just melted. The severity of the compounding process is varied by varying the quantity of cooling water passing through the jacket or cored moving parts. The material in the Banbury is heated entirely by the frictional work done on it. The shearing forces are greatest, and therefore

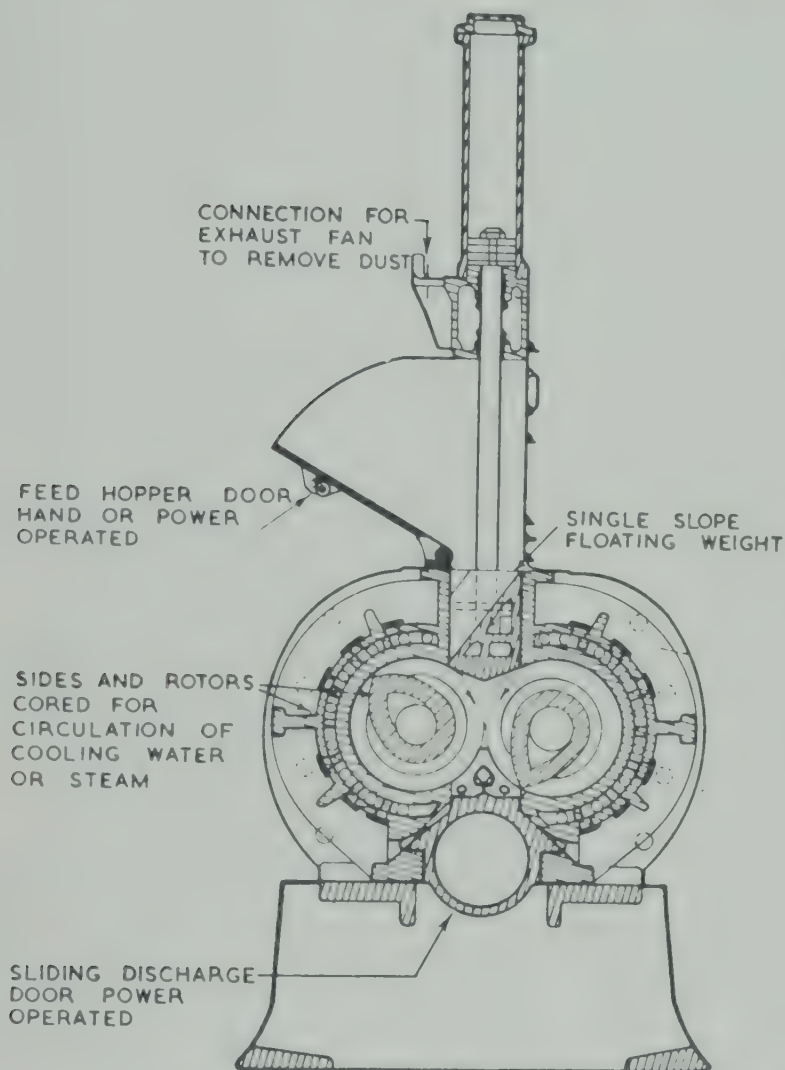


Fig. 4.1. Cross sectional drawing of Banbury mixer (Courtesy David Bridge & Co. Ltd.)

the compounding is most effective, when the polythene has just melted. Since the viscosity of the melt decreases with increasing temperature, the effectiveness of compounding is increased by lowering the rate of rise of temperature by the external application of cooling water and extending the cycle. The most effective dispersing is done in the temperature range

100°C–120°C and little useful purpose is served by prolonging the Banbury cycle once the melt temperature has reached 125°C. The Banbury is discharged by withdrawing the sliding door when the contents fall away leaving the chamber and rotors essentially clean. The charge is either deposited on to a mill whence it can be removed as a continuous strip and fed to a granulator, or is fed to an extruder which produces laces or strip for subsequent cutting.

With a rotor speed of 35 rev/min, when no cooling water is used at all, an overall cycle of 5 minutes can be achieved but this is generally found to be too short for adequate mixing. The use of maximum cooling water permits the cycle to be usefully extended to 12 or 15 minutes. In a 9 minute cycle the blending time before gelation is about 4 minutes and the actual compounding time about 5 minutes. The optimum cycle times have to be determined by trial and error for each compound.

In the preparation of coloured compounds it is generally advantageous to prepare first a master batch and then to dilute this by further compounding. This method of operation is found to give better pigment dispersion and to facilitate colour control in large scale operation. It is generally found that similar Banbury cycles can be used for the production of the master batch and the compound. The preparation of compounds for film extrusion can be simplified by first grinding the pigment with a suitable oil to eliminate agglomerates: the pigment paste is then used instead of a master batch. If the incorporation of an oil is considered undesirable, then it is necessary to ensure that the concentration of pigment in the master batch does not exceed 20% to give optimum dispersion in the final compound.

When compounding polythene with polyisobutylene or butyl rubber, it is again desirable to prepare an intermediate master batch containing approximately equal parts of each component. Higher final Banbury temperatures are used because the melt remains very viscous at high temperatures and more heat is generated. Also there is less risk of the material adhering to the rotors.

The granules of a fully compounded material should be quite homogeneous and a thin sheet compression moulded from them should be of uniform colour and intensity. Furthermore, if a microtomed section is cut from the granule and examined at a magnification of $100\times$ to $200\times$, the background of the field observed should appear uniform.

EXTRUDER COMPOUNDING

Most extruders in use at present have been designed to extrude finished sections as efficiently as possible*. They are able to melt polythene and pump it at a steady rate and uniform temperature through the die of the extruder. When most of the temperature rise of the polythene is due to heat conducted from the barrel this process can be carried out without vigorous mixing occurring in the melt. Under these conditions,

* See also Chapter 15

compounding is poor. When most of the heat is put into the polythene as a result of work done on the polythene in the extruder, then compounding is much more efficient. Extruders are generally unsuitable for the direct production of master batches due to the difficulty of accurate control of composition. Also most conventional extruders do not produce sufficiently high shear stresses to break down pigment agglomerates. As in the case of the Banbury mixer, the best pigment dispersions are obtained by using blends with masterbatches rather than dry pigment blends, but, unlike the Banbury mixer, an extruder cannot produce its own masterbatches.

Single screw extruders

In single screw extruders, good compounding conditions are best achieved by using screws whose length to diameter ratio is at least 15 : 1 and whose compression ratio is at least 2.5 : 1. With long screws of high compression ratio, the amount of work done on the polythene can become so great that cooling of the screw and barrel is necessary to prevent excessive rise of the temperature of the melt. Since in an extruder the polythene spends relatively little time in the temperature range 100–125°C, it is necessary to induce shearing stresses at higher temperatures when the polythene is less viscous by forcing it through narrow clearances such as occur in metering sections, smear heads and attrition discs or by passing it through mixing heads. These devices all add to the effectiveness of extruder compounding. It is essential that an extruder used for compounding should be adequately powered and, as a rough guide, the motor used should provide about 1 h.p. for every 5 lb per hour of output required. If the object is to produce from a blend of polythene and master batch a microscopically homogeneous compound, then it is generally necessary to pass the material twice through an orthodox extruder or to use an extruder specially modified for compounding. Such modifications usually result in the output of the extruder being appreciably lower than that expected when an orthodox extruder of the same size is used only for fabrication purposes.

Twin screw extruders

The standard intermeshing twin screw extruders used for extruding sections have not been designed specifically for use with polythene. Relatively little work is done on the polythene and most of the temperature rise of the polythene is due to transfer of heat from the barrel of the extruder. Under these conditions the use of mixing heads is even more necessary than with single screw extruders. The use of heavy filter packs is of assistance and homogeneous compounds can be produced by passing the material twice through these extruders as in the case of the orthodox single screw extruders.

Modified extruders

A number of specialized extruder compounders have been or are being developed for polythene compounding. The Welding Engineers compounding extruder (Plate 4.2) is a non-intermeshing twin screw machine

with screws of complicated design. This machine is known to produce a satisfactory dispersion of carbon black in polythene by a single pass extrusion of a blend of polythene and master batch. The Buss Ko-Kneader (Plate 4.3) is an ingenious machine in which a single screw with discontinuous deep flights rotates and reciprocates so that the flights of the screw intermesh with lugs fixed to the barrel and this again induces high shearing stresses. The barrel is made in two parts which open axially to facilitate cleaning. This machine has shown excellent promise for compounding polythene.

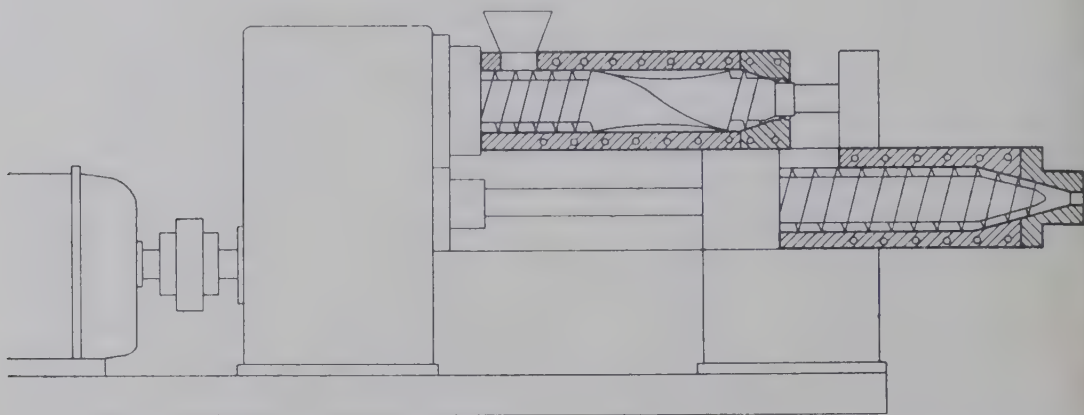


Fig. 4. 2. Diagrammatic representation of screws of the Eck Mixtruder (Courtesy Joseph Eck & Söhne)

Another novel machine is the Eck-Mixtruder (Fig. 4. 2). This machine is an intermeshing twin screw extruder but the screw thread only extends for one-third of the length of the screw and after the thread the extensions of the screw are somewhat similar in shape to the rotors of a Banbury mixer. This section is designed to produce a kneading-action and the aim here is to combine the principles of extruder and Banbury compounding. This machine can be fitted with a secondary single screw system which is fed directly from the end of the primary compounding section so that the extrusion of finished sections can be achieved in continuous operation. The Eck-Mixtruder is of considerable interest but requires further modifications to adapt it for use with polythene.

A COMPARISON OF THE BANBURY AND EXTRUDER COMPOUNDING PROCESSES

The advantages of Banbury compounding lie in the versatility of the process. The effective cycle time can be varied over a considerable range. Pigment agglomerates can be broken down effectively because very high shear stresses are developed. There is no large scale blending problem and any number of components can be fed to the Banbury. The form of the additives or polythene is not critical and liquids can be incorporated if desired. All parts of the machine are accessible for cleaning purposes so that colour changing is relatively straightforward.

The disadvantages of the Banbury process are that it is difficult to exclude atmospheric contamination and to prevent oil contamination

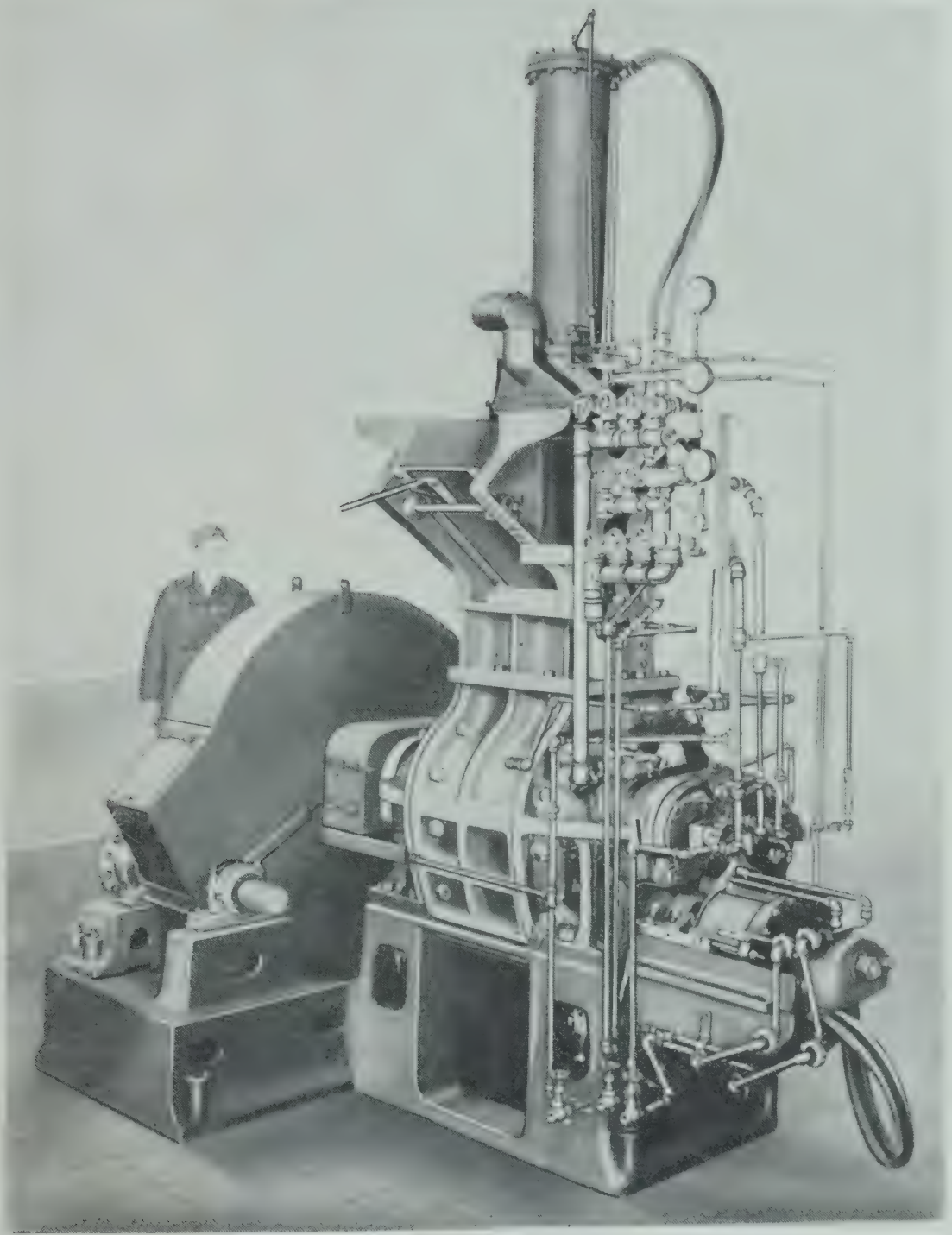


Plate 4.1. Standard type of Banbury mixer (Courtesy David Bridge & Co. Ltd.)

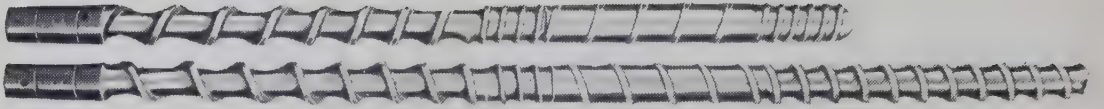


Plate 4.2. Screws of the compounding extruder by Welding Engineers, Inc.

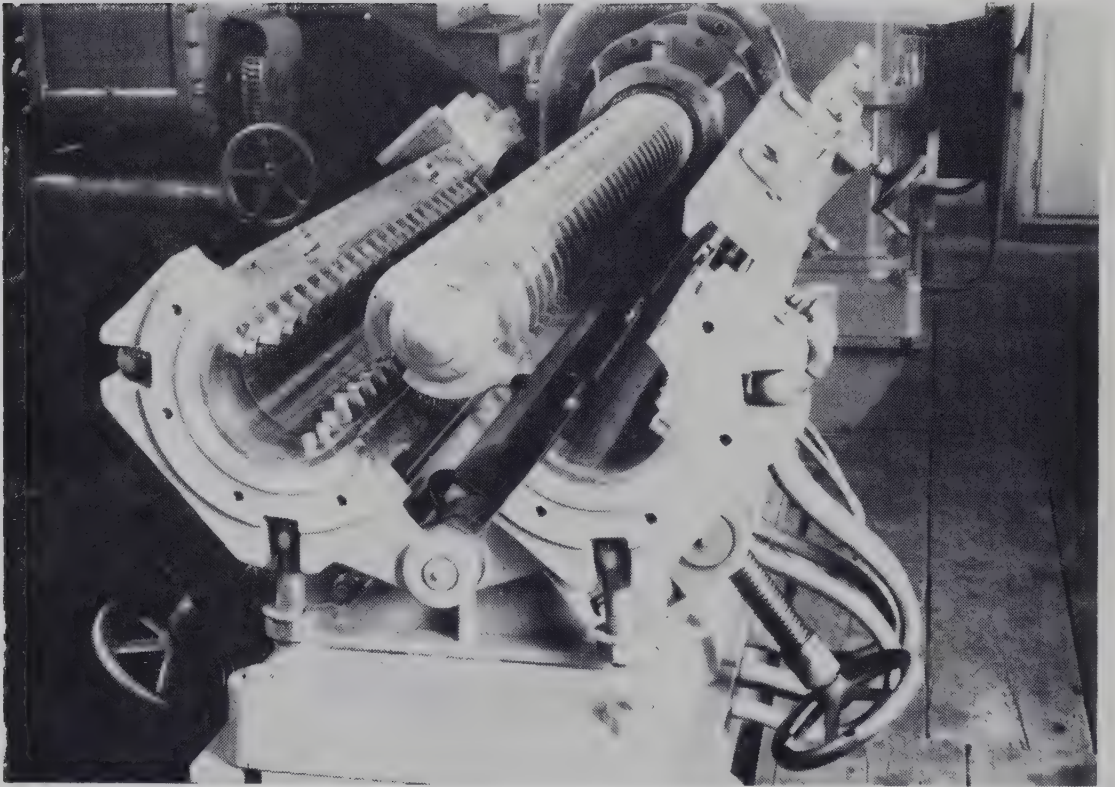


Plate 4.3. The Buss Ko-Kneader (Courtesy Buss A.G.)

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when the machine is discharged. While batchwise operation simplifies the problem of blending it does necessitate more manual control than is required for an extruder compounder.

The advantages of using an extrusion system for compounding are that little manual control is required, contamination is easily prevented, and the product is easily handled by die face, spaghetti or cube cutting techniques. Furthermore, the process is continuous and this ensures that all granules of the product have identical thermal histories. The disadvantages are associated with the difficulties of colour changing and producing homogeneity, with the restriction on the form in which the materials can be fed to the extruders and with the fact that extruders are unsuitable for producing masterbatches.. Colour changing is, of course, greatly simplified if spare screws and heads are available and can be easily interchanged.

The selection of one or other process will be determined by considerations of the economics of the respective processes and the variety of products which have to be manufactured.

COMPOUNDING DURING FABRICATION

The quality of dispersion required in the end product determines whether or not a compound should be used. Thus, in the highly competitive field of injection moulded products, the additional cost of a prior process is generally undesirable and adequate dispersions of pigments can be obtained by simply feeding dry tumbled blends of pigments and polythene to the injection press. This technique is satisfactory because the question of filter blockage does not arise and the quality of the product is assessed only on visual appearance. A much finer dispersion of pigment giving a product of superior appearance would, of course, be obtained if a compound were fed to the machine instead of a blend. The use of a master batch blend instead of a dry pigment blend, however, would generally only produce a mottled moulding since little mixing occurs in the cylinder of the injection press.

The use of dry pigment blends is generally unsatisfactory for extrusion processes. This is because the pigments tend to agglomerate and this results in rapid filter blockage and causes tearing in film production and electrical failure in the case of cable insulation. Satisfactory coloured film can be extruded by feeding a blend of master batch and polythene provided that the master batch is specially prepared and that adequate mixing occurs in the extruder. When cable insulations are coloured for identification purposes only, then a satisfactory product can again be obtained by feeding the extruder with a blend of polythene and master batch. Since the bulk of the production of polythene tube and external cable sheathing has to be capable of withstanding outdoor exposure for many years, it is essential that these products contain 2%–3% of channel carbon black finely dispersed. When a microtomed section of tube or sheath is examined under the microscope it must be free of areas or

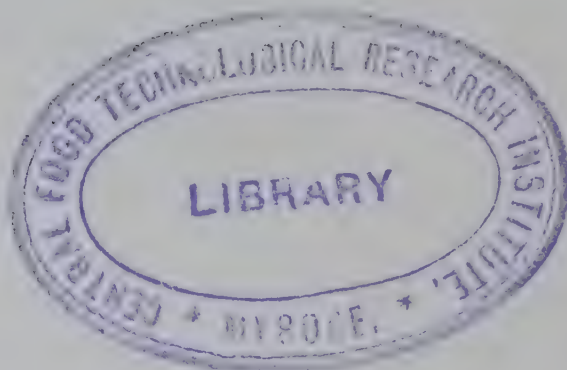
streaks containing little or no carbon black since degradation would otherwise occur on subsequent exposure at points where these areas extend to the surface.* It is not generally possible to produce an adequate dispersion of carbon black by a single extrusion of a blend of polythene with carbon black master batch. Thus for cable extrusion it is essential to use a compound, while for tube extrusion it is desirable to use a compound or to granulate the product of the first pass through the extruder and use this for extruding the finished tube.

Compounding of high density polythene

The foregoing discussion refers to the compounding of conventional polythenes of density approximately 0.92 which have been in use for many years. The same comments would in general apply to the compounding of the newer high density polythenes except that any temperatures quoted would be raised by about 20°C.

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 Bernhardt, L. C., and McKelvey, J. M., "Application of adiabatic techniques to polyethylene extrusion", Pt. I, *Rubber World*, 130, 513 (July, 1954). Pt. II, *Rubber World*, 130, 655 (Aug., 1954).



* See Chapters 6 & 11

CHAPTER 5

PIGMENTATION

E. J. G. BALLEY AND R. W. GOULD

THE natural appearance of polythene is not one of its attractive features, and thus the popularity of this material in the domestic and toy markets is to no small extent due to the way in which it can be coloured attractively. In industrial applications polythene is often coloured for identification purposes and for providing good weathering characteristics. The colours which are available in polythene are limited to the opaque and translucent ranges because of the waxy or milky appearance of the natural polymer.

At first sight the colouring of polythene appears to be comparatively simple in view of its inert nature. In practice however, there is available a restricted range of colourants which are completely stable in polythene during manufacture and in use, and which do not react to give undesirable effects. The processes for colouring polythene to produce the best results have to be carefully chosen so as to obtain satisfactory dispersion of pigments. This arises because of the comparatively narrow margin between the temperature at which the mix is molten and the one at which it has become so fluid that no further breakdown of pigment agglomerates can take place. For applications where complete uniformity of colouring is not required, simple operations are available.

COLOURING PROCESSES

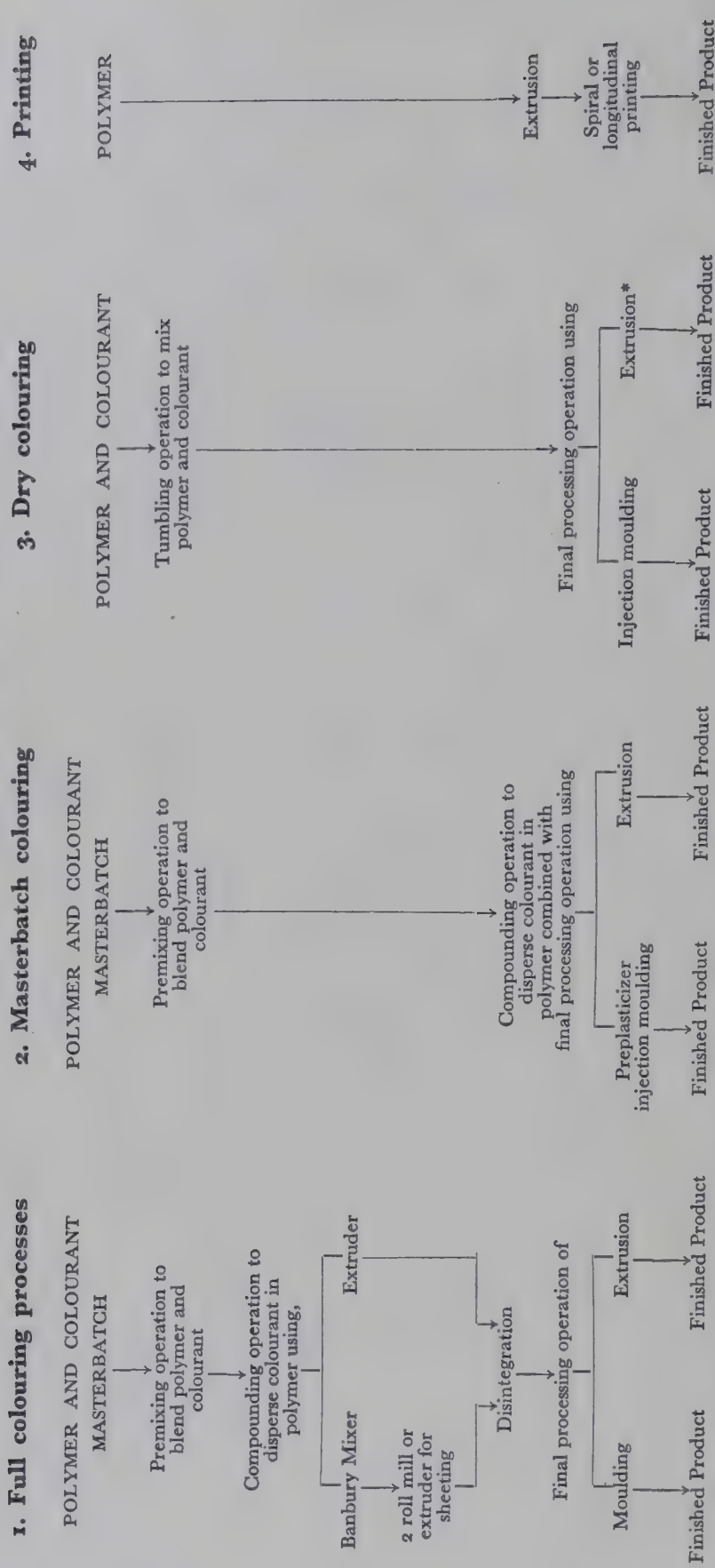
The various ways in which coloured polythene mouldings or extrusions can be made are illustrated in Fig. 5.1, starting with the elaborate ones designed to give the highest quality of dispersion on the left, and moving through the more simplified processes to the right. In the interests of production costs it is desirable to use the simplest process which will give a product of the required quality. The methods of operating these processes have been described in Chapter 4, and typical circumstances when a particular process is appropriate can be summarised as follows.

Method 1 (in Fig. 5.1) should invariably be used when it is necessary to have as perfect a dispersion as possible. It should be used in such instances as the production of: black or brown compounds with good weathering characteristics, where the performance is directly proportional to the degree of dispersion; compounds of high electrical quality, where, again, poorly dispersed colourants impair performance; compounds intended for film or monofilament extrusion, where pigment agglomerates

3829

15.3.58

Fig. 5.1. Typical methods for colouring polythene



* The orthodox extruder may not provide adequate distribution of pigment unless the product is disintegrated and re-extruded. A mixer-extruder may be required for direct preparation of a finished product. It may be also necessary to select pigments which do not cause blocking of the filters of the extruder.

PIGMENTATION

can cause tearing and low output through blocking the filters; and pigment masterbatches.

Method 2 can be adopted when all that is required is that the mouldings or extrusion should be of uniform colour.

Method 3 can be used when complete uniformity of colouring is not required. This method may also be used with colourant masterbatch instead of colourant for the deliberate production of mouldings containing streaks of colour.

Method 4 is sometimes used for colour identification on wires insulated with polythene, but the relatively poor adhesion between ink and polythene detracts from the value of this method. Polythene can also be readily surface dyed using acetate rayon dyes but because these colourants are soluble in the polythene they fade and tend to migrate or bleed to other articles.¹

The colourant masterbatches referred to in the table are concentrated dispersions of pigment in polythene and are of such a strength that 3–5 % is used to obtain the final colour, but masterbatches intended for the production of film are frequently more dilute than this in order to facilitate dispersion. As an alternative to a masterbatch in polythene, dispersions of pigment in a mineral oil (for example, liquid paraffin) are sometimes employed. No incompatibility (sweating) will be observed, provided not more than 2 % mineral oil is present in the final mix, but formulations containing mineral oils degrade electrically upon ageing.²

REQUIREMENTS OF COLOURANT

A colourant which is to be considered suitable for use in polythene should ideally conform to the following requirements:

It should disperse readily during normal processing.

It should be stable to processing and subsequent moulding or extrusion where the compound may be held at temperatures of up to 250°C (480°F) for as long as $\frac{1}{2}$ hour or at temperatures of up to 300°C (570°F) for a few minutes.

It should, over the range of concentrations and temperatures likely to be used, be insoluble in the polymer or any other component of the mix, as solubility will allow migration of colour.

It should not catalyze oxidation or degradation of the polymer so as to cause embrittlement or the formation of odour or gelled particles.

It should not cause significant deterioration of the thermal, electrical or weathering characteristics of the polymer.

It should give colours of good light stability.

Dispersion

When polymer and colourant are processed together it is important that there should be as uniform a mixture as possible of the two components (i.e. that there should be good distribution of colour) and it is also desirable that all pigment agglomerates should be completely broken down (i.e. that the dispersion should be as complete as possible). Certain

inorganic pigments tend to agglomerate on storage, particularly in damp conditions, and in severe cases may reach the stage where the pigment will not disperse satisfactorily under normal processing conditions.

Heat stability

Some colourants are insufficiently stable to withstand being heated in polythene and as a result they fade, darken or change in colour during compounding or subsequent processing. Those which can be used without restriction in polythene must be capable of withstanding $1\frac{1}{2}$ hours heating in a closed mould at 250°C (480°F), though for simple moulding processes colourants which are stable for 15 min. at 240°C (465°F) may be satisfactory. An alternative, but slightly more exacting test, to $1\frac{1}{2}$ hours at 250°C , consists of heating the material at 310°C (590°F) in a closed mould for 3 minutes², but this eliminates most organic colourants, some of which may be satisfactory in practice. Colourants which are claimed² to withstand the test at 310°C include:—iron oxides (calcined), cadmium sulphides, cadmium sulpho selenides, certain metallic phthalocyanine greens and blues, chromic oxides (anhydrous), carbon blacks (channel), titanium dioxide (anatase and rutile), zinc oxide.

Colour migration

Solubility of the colourant in polythene or one of the other components of the mix, can give rise to the formation of a coloured surface bloom or can allow the migration of colourant from the coloured formulation to other materials with which it may be in contact. The circumstances in which these faults may occur are as follows.

Blooming. Blooming, which is the formation of a film of dry colourant on the surface of the polythene product, results from the formation of a super-saturated solution of colourant in the polymer or other component of the mix during compounding, with subsequent slow recrystallization on the surface of the finished product. Blooming may not begin to develop for a considerable time after processing and its severity is not necessarily a direct function of colourant concentration.²

Bleeding. Bleeding, which is the migration of colourant in solution, is distinct from blooming because, while both cause colouring of other materials with which the product is in contact, no colourant can be rubbed from the surface of sample which is exhibiting bleeding alone. When bleeding occurs, its severity is usually proportional to the concentration of colourant.

Bleeding will occur readily when the colourant is soluble in polythene and can thus migrate into a second material in which it is also soluble. A less serious form of bleeding can also take place with colourants which are insoluble in polythene, through extraction by materials in which they are soluble.

A simple test for eliminating colourants which bleed in polythene is made by checking their solubility in toluene or xylene at room temperature. Colourants which are markedly soluble in the cold can be dis-

carded without further study. On the other hand, several which appear to be insoluble will dissolve in polythene at processing temperatures and will therefore bleed and may also bloom.

Catalytic effect

Some colourants will induce catalytic oxidation or degradation of polythene during processing or on storage. The faults which may occur during processing are the formation of nodules of gelled or more viscous material, or the development of odour. The action of the colourant during storage can result in embrittlement or the development of odour or both.

These catalytic effects can occur with pigments based on cadmium, cobalt or manganese, and Goodwin² has reported that hydrated chromic oxide causes embrittlement on storage, and that iron blues promote both odour and embrittlement.

The inclusion of antioxidants in the polythene mix reduces or prevents these reactions.

Electrical characteristics

The electrical characteristics of polythene are modified by the inclusion of colourants and in critical applications the effect on the power factor for even small inclusions can be quite serious.

The incorporation of 2% carbon black increases the power factor but the value remains steady even after 2,000 hours ageing at 105°C. Rose ultramarines also increase the power factor initially but the effect diminishes on ageing at 105°C and the pigment then becomes one of the more stable.

Pigments which cause a rapid rise in power factor on ageing include the cobalt blues. Those which have some stabilizing action include the cadmium yellows, oranges and reds and certain phthalocyanines.

Light stability and weathering characteristics

The light stability of a coloured polythene is not usually as high as for a corresponding formulation in other neutral plastics, such as acrylic sheet. The behaviour of a pigment can frequently be predicted from its known behaviour in other chemically unreactive plastics. As with other plastics materials, polythene formulations containing small proportions of colourant, or tints based on opaque white, have limited light stability and will fade to a greater extent than full strength shades.

The failure of natural polythene to withstand weathering is characterized by loss of flexibility, the development of surface cracks and ultimate brittleness. Other properties which are markedly affected even before surface cracks or general brittleness can be observed include low temperature brittleness, elongation at break, power factor and surface resistivity.³

While most pigments have no influence on the weathering of polythene a few cause it to degrade prematurely while others protect it. The most notable example of those which protect is carbon black, and a compound containing 2% of a fine particle channel black has extremely

good weathering properties. The carbon black should have a particle size of 30 millimicrons or less, and should be well dispersed. Suitable methods of testing the dispersion are described in the literature^{3, 4} and Chapter 6. Other pigments which have some protective action include Monastral fast blue BS, the Irgalite yellows WSC and WSR⁵, and a brown formulation containing chrome molybdate orange and carbon black.²

* COLOURANTS FOR POLYTHENE

By now it is well accepted that only a few of the different classes of dyestuffs and pigments are of value in colouring any one plastics material and to this generalization, polythene is no exception. In fact, of the nine classes of organic colourants which will later be discussed, only three are of any real interest.

Colourants can be divided into the two groups of dyestuff and pigment under the following definitions.

Dyestuffs are completely soluble in the medium in which they are applied. All known types of dyestuff, both natural and synthetic, are organic in nature, and their full tinctorial value is only apparent when the colourant is in solution.

Pigments are essentially insoluble in the medium in which they are employed, and they can be divided into two main groups: inorganic colours, both natural and synthetic; and organic, which are synthetic.

Table 5.1. COMPARISON OF PROPERTIES FOR ORGANIC AND INORGANIC COLOURANTS IN POLYTHENE

Property	Organic	Inorganic
Tinctorial strength	High	Comparatively weak.
Cost	Cheap in use due mainly to high tinctorial strength	Some synthetically produced types are expensive to use because of their low tinctorial strength.
Colour and range available	Available in an extensive range of bright colours	More limited range which, with one or two notable exceptions, are rather duller than organic colours, particularly in reduced shades.
Light stability	With the exception of one or two particular classes, have poorer light stability than inorganic colours	Generally have excellent light stability.
Heat stability	Few types are stable above 250°C	Most anhydrous types are stable at much higher temperatures.
Migration	Many types exhibit characteristics which may cause migration	Do not migrate.

PIGMENTATION

When considering colourants for plastics, however, it is more satisfactory to classify them thus: organic dyes and pigments and inorganic pigments. Within these two classes there exists a wide variety of different chemical types, each having its own particular characteristics, but in spite of this, the organic and inorganic families when incorporated in polythene exhibit a number of typical properties which are listed in Table 5.1.

A discussion of the nature and properties of the various available types of both inorganic and organic colouring matters is given below, with particular reference to their suitability for use in polythene. Tables 5.2 and 5.3 give typical examples of satisfactory colourants.

INORGANIC PIGMENTS

Table 5.2 lists the properties of typical inorganic colours which are suitable for polythene, separated according to the classes discussed below. This list is intended to give examples only: it is by no means exclusive.

Carbon black. Carbon black is cheap, inert, stable to light and heat, and can be produced in a finely divided condition.

Gas black (channel black)—is relatively pure carbon of extremely fine dimensions, obtained by burning hydrocarbon gases in an insufficient supply of air. It has an intense black colour, great staining power and gives a brownish-black on reduction. The protection given to polythene by a well dispersed channel type carbon black has already been mentioned.

Lampblack or vegetable black is not such pure carbon as gas black and is obtained from the incomplete combustion of oils. It is of a deep black shade giving bluish-blacks on reduction.

Mineral blacks are earths containing up to about 60% of carbonaceous matter and a high proportion of silicious matter. Because of their low carbon content, these blacks have comparatively poor staining power.

White pigments. White pigments are used to contribute both whiteness and opacity to the particular material into which they are incorporated. Thus their chief requirements are that they should be opaque and have good covering power.

There are two white pigments which have satisfactory properties in polythene, titanium dioxide and zinc oxide. Titanium dioxide which exists in two crystalline forms, anatase and rutile, is superior in opacity and covering power. Anatase, which was the first form to be manufactured commercially, chalks on weathering; the rutile form, which is very slightly more yellow than the anatase, does not suffer from this defect and has the advantages of slightly greater covering power and higher total reflectance.

Pure zinc oxide is a brilliant, pure white pigment which is heat and light stable, and which does not chalk in polythene. It has the disadvantage of considerably lower covering power than titanium dioxide,

Table 5.2. TYPICAL INORGANIC COLOURS FOR POLYTHENE

Class and commercial name	Supplier in the U.K.	Colours obtained	Trans- parency	Light stability		Remarks
				Full shade	Reduced shade	
<i>Carbon</i> Kosmink carbon black	Chance & Hunt Ltd.	Blacks and neutral greys		Excellent	Excellent	Suitable for the preparation of compounds of good weathering properties.
<i>White pigments</i> Rutiox CR Anatase HR Zinc oxide-Red Seal	British Titan Products Ltd. British Titan Products Ltd. Durham Raw Materials Ltd.	Non-chalking whites Whites Non-chalking whites	Opaque Opaque Opaque	Excellent Chalks out-of-doors Excellent	Excellent Excellent	
<i>Iron oxides</i> Deanox red L10 Indian 11436 Burnt sienna CC 59431 M	Morris Ashby Ltd. Derby Oxide & Colour Co. Golden Valley Colours Ltd.	Reddish-browns Dull bluish reds Reddish-browns	Opaque Opaque Opaque	Excellent Excellent Excellent	Excellent Excellent Excellent	
<i>Cadmium pigments and lithopones</i> Cadmium maroon DC720	Blythe Colour Works Ltd.	Deep maroons, Dull in reduced shades	Opaque	Excellent	Excellent	
Cadmium lithopone P574 Cadmium pigment P410 Cadmium light yellow DC547	Johnson Matthey & Co. Ltd. Johnson Matthey & Co. Ltd. Blythe Colour Works Ltd.	Mid reds Oranges Yellows	Opaque Opaque Opaque	Excellent Excellent Good	Good Good Moderate	The moderate light stability of this pigment in reduced shade is typical of cadmium yellows. Many chromes show a tendency to darken in certain atmospheres.
<i>Lead chromes and molybdates</i> Pure lemon chrome L3GS	Imperial Chemical Industries Ltd.	Lemon yellows	Opaque	Excellent	Excellent	
Pure middle chrome LGS Pure scarlet chrome YNS	Imperial Chemical Industries Ltd. Imperial Chemical Industries Ltd.	Mid yellows Yellowish reds	Opaque Opaque	Excellent Excellent	Excellent Excellent	
<i>Cobalt blues</i> Cobalt blue DC305 Cobalt blue 3196	Blythe Colour Works Ltd. Johnson Matthey & Co. Ltd.	Reddish blues Mid blues	Fair Fair	Excellent Excellent	Excellent Excellent	
<i>Ultramarines</i> Blue ultramarine RS6 Rose ultramarine RS12	Reckitts (Colours) Ltd. Reckitts (Colours) Ltd.	Blues Violets	Fair Fair	Excellent Excellent	Excellent Excellent	

is illustrated by the approximate amounts required to give identical covering:

Titanium dioxide—rutile	1.0
Titanium dioxide—anatase	1.2
Zinc oxide	7

Natural and synthetic iron oxides. Ferric oxide is widely used as a cheap red to brown pigment. In a calcined form it is sold as Turkey red oxide, Indian red oxide, Venetian red, rouge, etc., and in a hydrated form as yellow oxide. The completely anhydrous or calcined types have excellent properties in polythene, producing a range of dull red to brown colours of good stability and permanence. The hydrated types, on the other hand, are of no interest because they lose water during processing in polythene and change from their dull reddish yellow colour to brown.

Natural iron oxides which are diluted with silica and other substances are known commercially as siennas and ochres. When these contain a relatively high proportion of manganese dioxide they are called umbers. The colours of many of these earths can be reddened by calcination when they are said to be "burnt". As with the synthetic oxides, only the anhydrous or burnt types are of any interest in polythene. Umbers or other oxides which contain a large percentage of manganese may cause the development of odour during processing. Natural oxides must be finely ground in order to obtain consistency and adequate dispersion.

Cadmium pigments. Cadmium pigments are available in a wide range of bright yellow, through orange, to crimson shades, but they are expensive. They consist basically of cadmium sulphide and cadmium sulpho-selenide. The shade of the cadmium sulphide yellows depends upon the method of preparation and the proportion of zinc sulphide present, and varies from lemon yellow to orange. Compounds of cadmium sulphide and cadmium sulpho-selenide in varying proportions form a further series of colours covering a range from orange to deep crimson, according to their composition. A series of pigments known as cadmium lithopones are also produced in which cadmium sulphide or sulpho-selenide is coprecipitated with barium sulphate. On account of their comparatively low cost tinctorially, these lithopones lend themselves to wider industrial application than the parent cadmium pigments.

Both cadmium pigments and cadmium lithopones have excellent properties in polythene and permit the production of an extensive range of bright yellow to crimson shades, though the reduced shades of the bluer-red and deep crimson types tend to be rather dull. The colours produced are stable to the effects of light, heat and chemical attack and are recommended for use when their high cost can be tolerated.

When used in film compounds, cadmium pigments tend to promote oxidation of the polymer under the high processing temperatures involved unless a suitable anti-oxidant is included.

Chrome yellows and molybdate oranges or scarlet chromes. These consist basically of lead chromate and cover a variety of shades ranging from a

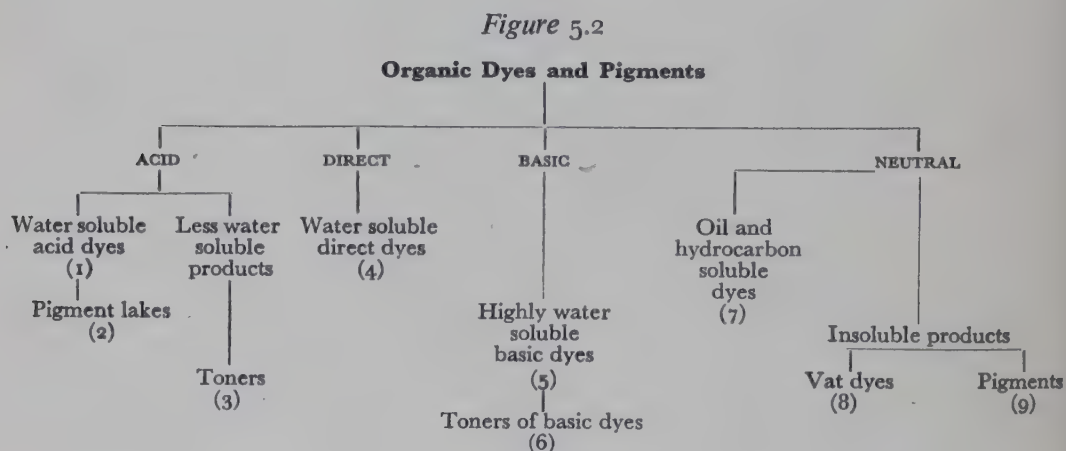
pale primrose to a deep orange-red. The primrose shades consists of mixed crystals of lead chromate and lead sulphate. The deeper yellow shades owe their colour to the presence of basic lead chromates, but the physical state of the pigment also plays an important part. The orange-red or scarlet shades contain up to 10 % of lead molybdate.

The lemon shades possess excellent covering power, but this property diminishes slightly as the shade reddens until the scarlet shades are reached, when it is regained. The heat stability of these pigments (particularly the orange to scarlet types) is satisfactory for general moulding operations, but they are not recommended where exacting heat stability is required, such as in the manufacture of film. On exposure in certain atmospheres these pigments tend to darken.

Chromium oxide. Chromium oxide (Cr_2O_3) is an extremely permanent green pigment, but it is difficult to obtain in a form ground finely enough to ensure adequate dispersion in polythene. It produces dull colours of exceptional fastness to light and heat.

A hydrated form known as Viridian or Guinet's green, which has the advantage of having a smaller particle size, is of no interest in polythene because of insufficient heat stability.

Cobalt blues. Cobalt blues consist essentially of a solid solution of cobaltous oxide in aluminium hydroxide and are available in a range of



shades from a greenish-blue, which may contain combined chromium, to a reddish blue. They produce very pure shades of blue of good translucency, stable to light and heat. The coarser grades tend to agglomerate when damp and may prove difficult to disperse when using a dry colouring technique. When finely ground the cobalt blues disperse much more readily, but fine grinding makes them lose their tinctorial strength. They also tend to promote the formation of odour.

Ultramarines. Ultramarine blue is essentially a polysulphide of sodium aluminosilicate, and occurs naturally as lapis lazuli. It is made by

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alcining mixtures of kaolin, silica, sodium carbonate, sulphur and resin in a muffle furnace. Its shade depends on the particle size to which it is ground.

Violet or rose ultramarines are prepared from blue ultramarines by treatment with hydrochloric acid gas at about 275°C.

Ultramarines produce a limited but useful range of reddish-blue to violet shades which have good light and heat stability in polythene. They disperse readily, but have little covering power and produce shades of moderate translucency. The tinctorial strengths become increasingly less with increasing redness of shade.

On reduction with white the greener shades become progressively greener (i.e. have green undertones) whilst red shades become progressively redder (i.e. have red undertones).

ORGANIC DYES AND PIGMENTS

A classification, useful to the plastics industry in which organic colouring matters are divided into nine classes, is given in Fig. 5.2.

Of these nine classes only three (namely, toners, vat dyes and pigments) contain colourants which are of interest for polythene.

A brief description of the nine classes and the reasons why six of them are unsuitable are given below. It must be appreciated, however, that the generalizations which will be made, have been derived from a study of the behaviour of typical members in each group, and exceptions may hereafter be found.

In Table 5.3 there are listed the properties of some typical examples of the toner, vat dyes and organic pigment classes which are suitable for use with polythene. Once again, this list merely quotes examples and makes no claim to be exclusive.

Acid dyes. This class, along with the direct and basic dyes (classes 4 and 5, Fig. 5.2), depends on solubility for the development of the colour. When not in solution they have little or no pigment value and being insoluble in polythene, are therefore of no interest.

Pigment lakes. There are many forms of lake, but the type considered here is the product obtained when a water soluble acid dye is converted into an insoluble pigment by precipitating it on an inorganic base such as alumina or blanc-fixe. As a group, the lakes are not tinctorially strong because the base acts as a diluent; and, as their light stability is generally lower than that of organic pigments (class 9), they are of no particular interest in polythene.

Toners. Toners are forms of lake but differ from the type already mentioned in that there is no inorganic base present. Those considered here are the ones which are prepared from acid dyestuffs which have slight water solubility, by precipitating them as the insoluble calcium, barium or other salts. The metal present affects the shade of the final

Table 5.3. TYPICAL ORGANIC COLOURS FOR POLYTHENE

Class and commercial name	Supplier in the U.K.	Type	Colours obtained	Trans- parency	Light stability	
					Full shade	Reduced shade
<i>Toners</i>						
Irgalite yellow WSC	The Geigy Company Limited	Metallic salt of azo dyestuff	Greenish yellows	Good	Excellent	Excellent
Irgalite yellow WSR	The Geigy Company Limited	Metallic salt of azo dyestuff	Mid yellows. Pigment has green undertone	Good	Excellent	Excellent
Irgalite geranium F	The Geigy Company Limited	Metallic salt of azo dyestuff	Mid reds. Pigment has blue undertone	Good	Moderate	Moderate
Rubine toner BS	Imperial Chemical Industries Ltd.	Metallic salt of azo dyestuff	Mid reds. Pigment has slight blue undertone	Good	Moderate	Poor
Rubine toner 2BS	Imperial Chemical Industries Ltd.	Metallic salt of azo dyestuff	Bluish reds. Pigment has blue undertone	Good	Moderate	Poor
Irgalite crimson SCR	The Geigy Company Limited	Metallic salt of azo dyestuff	Bluish reds. Pigment has marked blue undertone	Good	Moderate	Poor
Rubine toner 4BS	Imperial Chemical Industries Ltd.	Metallic salt of azo dyestuff	Bluish reds. Pigment has marked blue undertone	Good	Moderate	Poor
Polymon violet RS	Imperial Chemical Industries Ltd.		Bluish reds. Pigment has marked blue undertone	Good	Moderate	Poor
Polymon violet BS	Imperial Chemical Industries Ltd.		Reddish violets	Good	Moderate	Very poor
<i>Vat dyes</i>						
Irgalite blue 2RS	The Geigy Company Limited	Anthraquinone	Reddish blues	Good	Good	Good
Polymon blue 3RS	Imperial Chemical Industries Ltd.	Anthraquinone	Reddish blues	Good	Good	Good
<i>Pigments</i>						
Irgalite yellow BR	The Geigy Company Limited	Benzidine	Mid yellows. Pigment has green undertone	Good	Moderate	Poor
Vulcafor fast yellow 2GS	Imperial Chemical Industries Ltd.	Benzidine	Mid yellows. Pigment has green undertone	Good	Moderate	Poor
Polymon yellow RS	Imperial Chemical Industries Ltd.		Reddish yellows in full shade, greenish yellows in reduced shades	Good	Good	Moderate
Irgalite orange F2G	The Geigy Company Limited	Modified benzidine	Reddish oranges	Good	Moderate	Moderate
Irgachrome brown T	The Geigy Company Limited	Modified chrome	Mid brown	Opaque	Excellent	Excellent
Irgalite fast red PY	The Geigy Company Limited	Parazalone red	Mid red	Good	Good	Moderate
Irgalite fast brilliant blue BL	The Geigy Company Limited	Copper phthalocyanine	Mid blues	Good	Excellent	Moderate
Polymon blue BS	Imperial Chemical Industries Ltd.	Copper phthalocyanine	Mid blues	Good	Excellent	Excellent
Irgalite fast brilliant green GL	The Geigy Company Limited	Chlorinated copper phthalocyanine	Bluish greens	Good	Excellent	Excellent
Polymon green GS	Imperial Chemical Industries Ltd.	Chlorinated copper phthalocyanine	Bluish greens	Good	Excellent	Excellent
Irgalite green BS	The Geigy Company Limited	Modified copper phthalocyanine	Mid greens	Good	Excellent	Excellent
Irgalite green BYS	The Geigy Company Limited	Modified copper phthalocyanine	Mid greens	Good	Excellent	Excellent
Polymon green YS	Imperial Chemical Industries Ltd.	Aniline black	Yellow greens	Good	Excellent	Good
Irgalite black SN	The Geigy Company Limited	Aniline black	Black and bluish greys	Good	Excellent	Excellent
Monolite fast black BS	Imperial Chemical Industries Ltd.	Aniline black	Black and bluish greys	Good	Excellent	Excellent

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pigment, for example barium red toners are more yellow than calcium and manganese, which are progressively more blue.

Toners are intense colourants, which, by virtue of their lack of base will yield highly translucent effects. As a class they are not extremely fast to light, but they can have completely non-migratory properties and excellent heat stability in polythene. Toners thus form a very important class of colourants for polythene.

Direct dyes and Basic dyes. For the reasons given under *Acid dyes*, above, these two classes of colourants are of no interest in polythene.

Toners of basic dyes. This class of toner is formed from the basic dyes by combination with phospho-molybdic and/or phospho-tungstic acid. They are insoluble coloured compounds, which are not particularly light stable, although they are superior to the dyes from which they have been formed. Their heat stability is however so poor that their application in polythene is severely limited.

Dyes soluble in oils, hydrocarbons, esters and ketones. This class of dyestuff embraces a wide variety of chemical types such as the simple mono-azos and anthraquinones as well as the more complex acetate-rayon speciality colours. Those highly soluble in polythene and hydrocarbons can exhibit serious colourant migration as blooming and bleeding and hence are of little value. Many members of this class are also rather unstable to light.

Vat dyes. These are insoluble organic dyes of the anthraquinone or indigoid class which are used in textile work by first making them soluble in water by reduction and, after dyeing, oxidizing them to insoluble pigments. Most vat dyes cannot be used as pigments because they suffer from defects such as high cost, poor dispersion, migration and lack of stability. However a few are sufficiently fast to heat and light and have the requisite non-migratory properties to be of interest in polythene, but for this purpose they must be specially manufactured.

Organic pigments. These comprise a large group of organic colours containing little or no metallic constituent. Grouped under this heading are a variety of chemical compounds, including the red, orange, and yellow azos and the blue and green phthalocyanines.

Careful choice of these colours must be made for polythene, since many members show some solubility at processing temperatures. Those free from this defect show a good standard of stability to light and heat, coupled with high brightness and tinctorial strength. This applies particularly to the phthalocyanine class.

HIGH DENSITY POLYTHENE

The colouring of high density polythene presents no particular problem so far as the incorporation of pigment is concerned. This type of polymer does, however, require colouring materials of great heat stability, because the final processing operations are frequently carried out at temperatures

50°C higher than are used for normal polythene. In injection moulding for example, temperatures may exceed 300°C and, as heating periods of up to 20 minutes may be used, fewer colourants can safely be used with this type of polythene, than with the normal material.

When coloured high density polythenes are processed above 250°C, discoloration can take place, and this may be due to several causes, including: a discoloration of the polymer itself; a reaction between the polymer and the colourant which causes a partial or complete loss of colour; and the natural instability of the colourant at these high temperatures. These points are discussed below.

Discoloration of polymer. High density polythenes vary in the extent to which they discolour at high processing temperatures. Some will not discolour to an appreciable extent even after 30 minutes heating at 300°C, while others will turn brown after shorter periods of heat at lower temperatures, the extent of the discoloration depending on the temperature and time of heating. The discoloration is, of course, most serious for whites, blue and pale colours, such as creams. It is less serious for yellows, reds, greens and dark colours; and can pass unnoticed in oranges, browns and blacks.

Reaction between polymer and colourant. Some high density polythenes cause a premature breakdown of certain colourants, so that those which are normally stable for 30 minutes at 300°C, will change or completely lose their colour, even under less severe heating conditions. Some of the colourants listed in Tables 5.2 and 5.3 as being satisfactory for use in normal polythene, are subject to this form of attack and they include the chromes; the toners; and the pigments—Vulcafor yellow 2GS, Irgalite yellow BR, Polymon green YS, Irgalite orange F2G and Irgachrome brown T.

Instability of colourant to heat. Not all the dyes and pigments listed in Tables 5.2 and 5.3 as being suitable for normal polythene, are suffi-

Table 5.4. COLOURANTS, FOR HIGH DENSITY POLYTHENE, STABLE FOR 30 MINS. AT 300°C

Inorganic ^a	Organic ^b
Carbon blacks	Irgalite blue 2RS
Titanium whites	Polymon blue 3RS
Zinc oxides	Irgalite fast brilliant blue BL ^c
Cadmium yellows, oranges and reds	Polymon blue BS ^c
Iron oxides (as normally selected for polythene)	Irgalite fast brilliant green GL
Cobalt blues	Polymon green GS
Ultramarine blues and violets	Irgalite black SN
	Monolite fast black BS

^a See Table 5.2 for examples of each class.

^b See Table 5.3 for details of these colours.

^c It is normal for these pigments to lose intensity slightly at very high temperatures.

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ciently stable to be used at 300°C. The inorganic pigments which are not stable at 300°C are the chromes, which darken to varying extents above 250°C. The organic colourants in Table 5.3 which are not stable up to 300°C, are the toners and some of the pigments.

Pigments for high density polythene

The dyes and pigments which can be used for colouring unreactive high density polythene are listed in tables 5.4 and 5.5. Those which are

Table 5.5. COLOURANTS^a, FOR HIGH DENSITY POLYTHENE, OF LIMITED STABILITY

Colourant	Temperature
Irgalite yellow BR	250°C
Vulcafor fast yellow 2GS	250°C
Polymon yellow RS	260°C
Irgalite yellow WSC	260°C
Irgalite yellow WSR	260°C
Irgalite orange F2G	260°C
Irgalite geranium F	250°C
Rubine toner BS	280°C
Rubine toner 2BS	250°C
Rubine toner 4BS	250°C
Irgalite crimson SCR	250°C
Polymon green YS	290°C
Polymon violet RS	250°C
Irgachrome brown T	250°C

^a Details of these are given in Table 5.3.

particularly suitable because they are stable for 30 minutes at 300°C, are listed in Table 5.4.

In addition to the organic pigments listed in Table 5.4 there are others of lower stability which can be used with care in high density polythene. These are given in Table 5.5 along with the approximate temperature to which they are stable for 30 minutes in full colour in an unreactive polymer.

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CHAPTER 6

OXIDATION AND AGEING

C. K. HAYWOOD

IN the early days of the development of polythene it was soon established that means had to be found of protecting it from the effects of oxidation during ageing. Although a substantially pure hydrocarbon, polythene is susceptible to thermal and photo-activated oxidation which, if allowed to proceed unchecked, produces chemical and physical modification of the basic molecular structure resulting in marked deterioration of mechanical and physical properties.

Although the processes of heat and light degradation of unprotected polythene give rise to broadly the same end effect of embrittlement and rise of power factor, their prevention requires two different techniques. While a good antioxidant will extend the useful life of polythene many fold under conditions where the material is subjected to purely thermal oxidation, it will generally be quite ineffective where exposure to light is involved. Much effort has been devoted, both in England and in the U.S.A., to the study of these processes, perhaps the most notable being that of the Bell Telephone Laboratories. The approaches have been to follow the progress of thermal oxidation by measurement of power factor and oxygen uptake, and of photo-activated degradation by both accelerated tests and natural outdoor ageing trials. In the first case the marked inhibiting action of antioxidants has been conclusively shown, and in the latter the inclusion of a minimum of 2% of finely dispersed channel carbon black has protected polythene exposed to tropical sunshine for several years without serious deterioration compared with a life of less than six months for unprotected material exposed to the same conditions.

THE OXIDATION MECHANISM

Before proceeding to discuss the results of laboratory and outdoor ageing experiments it is of interest to outline the presently held theory of the mechanism of the oxidation process.^{1, 2, 3}

The polythene oxidation process follows an auto-catalytic curve, the rate increasing rapidly at elevated temperatures. As with lower molecular weight saturated aliphatic hydrocarbons, in which branched chain structures are more susceptible to oxidation, so polythene with its chain branching, as indicated by infra-red analysis, is prone to oxygen attack.⁴ Even in a completely unbranched polymer, some oxidative attack on the polythene chain would be anticipated, particularly at temperatures of 60°C and upwards. It would be expected that the high density polythenes would be less susceptible to oxidation than conventional low

density material because of their greater chain linearity. Tests on such products to date have not, however, so far shown any marked improvement in resistance to oxidation; this may be in part attributable to the impurity of the end product arising from the method of manufacture of these new forms of polythene.

While superior ageing properties might therefore be expected on theoretical grounds, detailed examination of chemically purer specimens will be necessary before the extent of such improvement can be assessed with any degree of certainty.

The mechanism of oxidation of polythene is considered to be similar to that for lower molecular weight aliphatic saturated hydrocarbons—a free radical propagating chain reaction. The process may be initiated by C—C or C—H bond rupture, or by direct attack by oxygen on the polymer chain, particularly where occasional unsaturated bonds may be present.

The free radicals so formed combine with oxygen yielding peroxide free radicals which then abstract a hydrogen atom from an adjacent hydrocarbon chain to form a hydroperoxide with simultaneous regeneration of a hydrocarbon radical. The process can then be repeated as a chain mechanism. Additionally, the hydroperoxide molecules can themselves dissociate into free radicals capable of propagating more extensive degradation through a branching mechanism.

Ultimately, as the result of both chain scission and decomposition of hydroperoxides giving rise to aldehydic and ketonic groupings, polythene is degraded to a brittle, low molecular weight material of high power factor. The production of short-chain fatty acids through side reactions is considered to account for the development in oxidised polythene of objectionable rancid odour. The above theory of an autocatalytic chain degradation process is directly supported by frequent measurement of the power factor of a sample of polythene exposed to an oxidising environment, the rise in this property, after an initial short induction period, being very rapid at temperatures in the region of 100°C and above. Similar rate processes have been found in corresponding oxygen uptake experiments.

The presence of an antioxidant has the effect of delaying this rise in power factor. Such agents, e.g. phenols and amines, function by substituting themselves, through transference of a hydrogen atom, for the more active hydrocarbon radicals.⁵ The antioxidant radical so formed is stabilised by resonance and is incapable of propagating the chain degradation to anything like the same extent. At moderate temperatures this inhibiting effect lasts for a long time, though once the antioxidant is exhausted rapid degradation develops. Limits are set to the amount of antioxidant which can be incorporated on grounds of compatibility with polythene and effect on physical properties. As a rule 0.1% to 0.2% is used where long term protection is required.

Although polythene, being a substantially saturated hydrocarbon, should not absorb in the visible or near ultra-violet, the presence of traces

of $C=O$ bonds enables the polymer to absorb radiation in this region starting at $3,300 \text{ \AA}$. and increasing rapidly to a maximum at $2,800 \text{ \AA}$.

Laboratory experiments using wave lengths outside the carbonyl absorption band did not cause oxidation, the results being confirmed by exposure trials under selected glass filters.

It will be seen from Fig. 6.1 that the intensity falls throughout the ultra-violet to zero at about $3,000 \text{ \AA}$. The position of this limit and the intensity near it are sensitive to latitude, the season of the year and atmospheric pollution. In summer the limit is about $2,950 \text{ \AA}$., but in the winter months it recedes to approximately $3,100 \text{ \AA}$., with an associated decrease in intensity near this limit. It is within this particular region that carbonyl group absorption begins to show a rapid increase

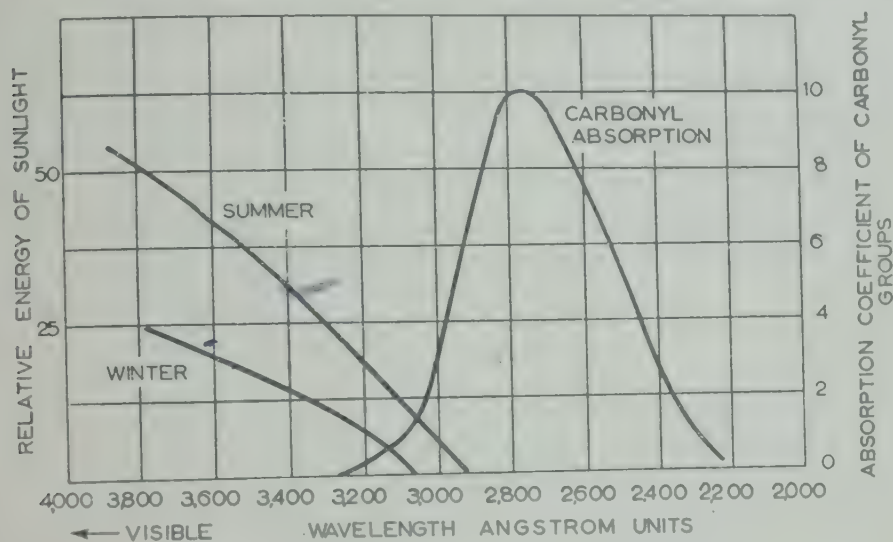


Fig. 6.1. Absorption of radiation by polythene

with decreasing wavelength. A shift of 100 \AA . towards the visible in the U.V. limit of solar radiation involves an approximately threefold decrease in carbonyl absorption, the total absorption being still further reduced by the associated seasonal decrease in intensity. It is this relationship which explains to a large extent the dependence of outdoor weathering of polythene upon the climate.

The carbonyl groups necessary for the initiation of photo-oxidation are derived from both the initial synthesis and subsequent fabrication conditions and as the result of normal temperature oxidation of unsaturated centres. Following light absorption, the oxidation mechanism is probably similar to that postulated for the thermal oxidation process, involving the production of free radicals of high activity and leading eventually to an increase in the overall carbonyl concentration. The process thus becomes autocatalytic, leading ultimately to poor mechanical properties, such as low elongation and embrittlement, and high power factor.

Antioxidants by themselves have been found incapable of preventing photo-oxidation. This is thought to arise from the very short length of

the oxidation chain coupled with the high rate of U.V. initiation of these chains, particularly in intense sunlight conditions.⁶ The antioxidant is itself affected and is also too immobile to migrate at a rate sufficient to affect the free radical chain mechanism. Polythene by itself is, in fact, sensitised to photo-degradation by the incorporation of aromatic amine, and to a less extent, phenolic antioxidant because of their relatively high absorptive power for ultra-violet radiation. In conjunction with an effective light screen however, the incorporation of such antioxidants to suppress the purely thermal oxidation does not constitute any hazard since together with the polythene they are protected by the screening additive from the effect of ultra-violet light.

Of the many ultra-violet absorbing agents examined only carbon black of fine particle size has withstood satisfactorily long term outdoor exposure tests under severe environmental conditions. Other substances have conferred a certain measure of protection, though to nothing like the same extent. While the pigmenting effect of carbon black is sometimes undesirable, it can be argued from fundamental principles that the prospect of finding an efficient, colourless, light stabiliser is remote, and that the best alternative to carbon black we may hope for lies in a dye-stuff possessing the right combination of properties.

EXPERIMENTAL STUDIES

Various methods have been used to follow the rates of oxidation of polythene. These include measurement of power factor at high frequencies,⁷ oxygen absorption¹ and carbonyl content by infra-red analysis.⁸ A correlation has been revealed between increase of power factor with increasing carbonyl content.⁹ The measurement of power factor to check the progress of oxidation is convenient, non-destructive and fairly rapid, and this property is sensitive to small changes. The values quoted have been obtained at 16 mc/s using the Hartshorn-Ward method on a Tinsley apparatus. Oxygen absorption measurements were made in a

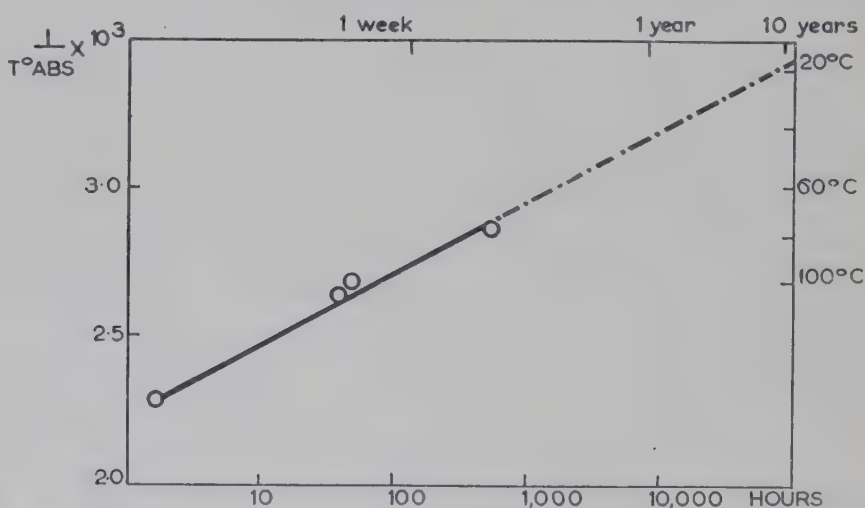


Fig. 6.2. Time for a power factor rise to 0.001 v. temperature for 40 mil polythene sheet in air

OXIDATION AND AGEING

modified Barcroft apparatus¹⁰ under approximately constant pressure conditions. The factors influencing the rate of oxidation are notably temperature, specimen thickness and presence of antioxidants and pigments.

Biggs has reported¹ that up to 90°C the rate of oxygen absorption is very low and this is substantiated by corresponding power factor measurements. Above 90°C the absorption rate increases rapidly showing marked change in rate in the region 90°–100°C. While this still corresponds to the solid state it is suggested that some connection may exist with the progressive reduction in crystallinity which begins to occur at these temperatures.

Tests carried out in aerated water at 95°C¹¹ have shown that unprotected samples of polythene of thickness 40 mils had become brittle and

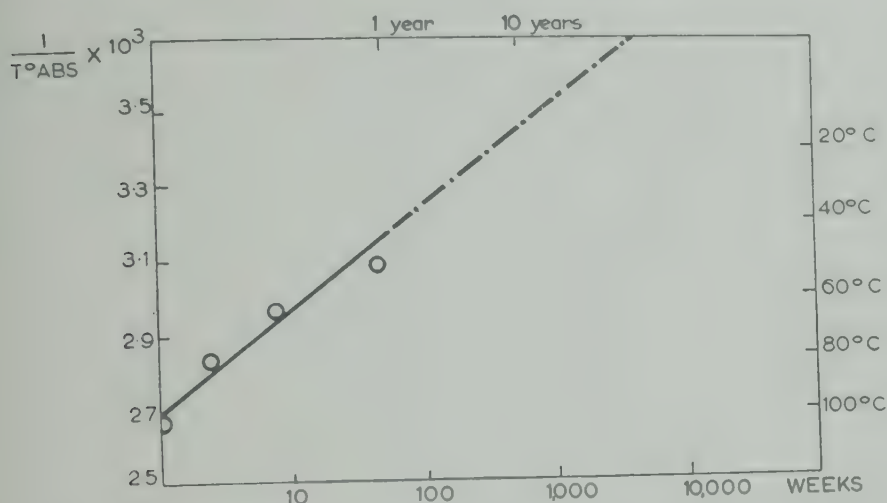


Fig. 6.3. Induction period v. temperature for 40 mil polythene sheet in air

the power factor greater than 0.001 after about 250 hours compared with 2 years for samples similarly exposed but at 50°C. In air alone at 105°C high power factor was developed after less than 500 hours, whereas an increase to only 0.0006 had occurred after 12,000 hours at 60°C.

Owing to the very slow rate of oxidation at normal temperatures estimates of the useful life of unprotected polythene under such conditions have so far been based upon extrapolations from data derived from shorter term tests at higher temperatures. Such estimates, though approximate, place the life of unprotected polythene maintained in the dark at 20°C in the region of 10–15 years. While these long extrapolations are subject to error and more complete information on behaviour at temperatures below 50°C is required to secure greater accuracy in the prediction of useful life, it is of interest to record¹ that a sample of polythene has been found to be unchanged in brittle point after 10 years storage in the dark at room temperature. Fig. 6.2 illustrates the time taken for the power factor to rise from 0.0002 (original value) to 0.001 for specimens of the same sample of polythene 40 mils thick exposed in air at 75°C, 100°C and 150°C. Time is plotted on a log scale against the reciprocal of the absolute temperature. Fig. 6.3 presents a similar plot

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of time to reach the commencement of measurable oxygen absorption in 40 mil sheets exposed to the air at temperatures of 100, 78, 65 and 50°

The effect of specimen thickness upon rate of oxidation is related to the rate of diffusion of oxygen through the solid. Up to thicknesses of

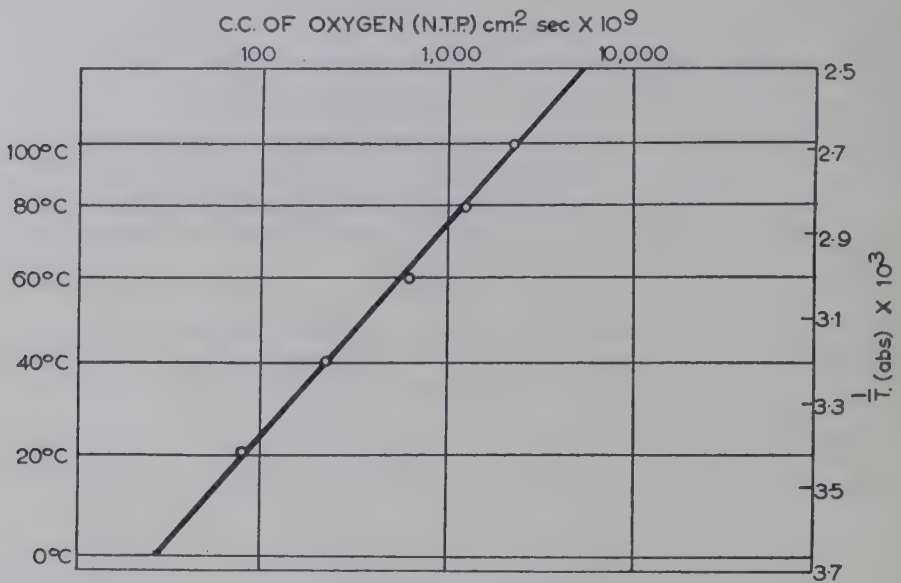


Fig. 6.4. Effect of temperature on the diffusion rate of oxygen into 0.25 in. thick polythene sheet in air

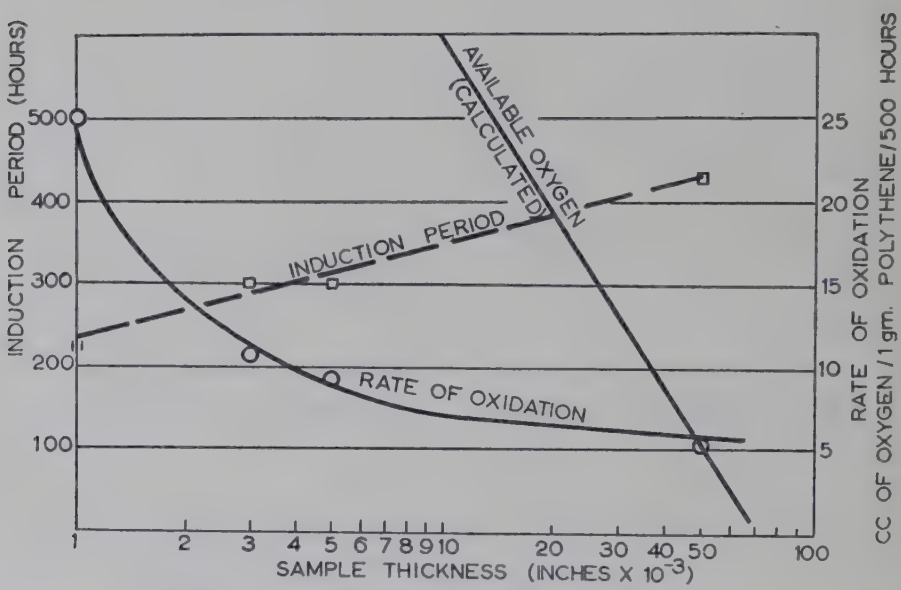


Fig. 6.5. Oxidation of polythene in air at 78°C

few mils the diffusion rate is not a major factor in determining the oxidation rate. Fig. 6.4 plots temperature against rate of diffusion of atmospheric oxygen into one side of a 250 mils thick sheet of polythene.

In Fig. 6.5 rates of oxidation at 78°C are plotted against sample thickness. The superposed plot of available oxygen at 78°C, calculated for different thicknesses from Fig. 6.4 shows that at 50 mils thickness and above the available oxygen within the specimen is insufficient to maintain

the oxidation rate. The induction period, as measured by the commencement of measurable oxygen absorption, is nearly twice as long for the 50 mils specimen as for the 1 mil specimen. The influence of thickness upon the overall rate of oxidation should therefore be taken into account in estimating the life of a particular polythene section.

The addition of pigments to polythene intended for electrical applications should be made with discretion. Certain metals (as described in Chapter 5), notably cobalt, show a pronounced adverse effect increasing considerably the proneness to oxidation. Such metals function catalytically and are to be avoided in the formation of coloured polythene compounds.

ANTIOXIDANTS

But for the availability of suitable antioxidants the use of polythene for dielectric applications would have been severely curtailed. Fortunately, prior investigations into oxidation inhibitors for rubber had made available several antioxidants, basically amines or phenols, which were found to be effective also in polythene. In general, protection against oxidation is required both during the compounding and processing stages at elevated temperatures and during subsequent service under normal or moderate temperature conditions.

For universal application the desirable properties an antioxidant should possess are as follows: capacity for inhibiting the oxidation of polythene under all practical temperature conditions; permanence, i.e. non-volatile and not extracted by water; complete compatibility with polythene; freedom from staining effects; no toxic hazard; freedom from odour.

Table 6.1. STRUCTURAL FORMULAE OF SOME ANTIOXIDANTS

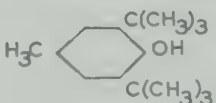
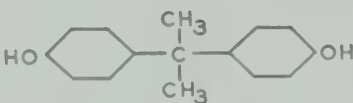


Chemical name	Structural formulae
2,6- <i>i</i> -butyl-4-methyl phenol	
Di- <i>o</i> -cresylol propane	
Diphenyl- <i>p</i> -phenylene diamine	
Di-β-naphthyl- <i>p</i> -phenylene diamine	

Table 6.2. VOLATILITIES OF SOME ANTIOXIDANTS

Antioxidant	Volatility at 180°C				% loss after 1 hr. at 240°C
	% loss after 1 hr.	2 hrs.	4 hrs.	24 hrs.	
di- β -naphthyl <i>p.</i> phenylene diamine	0.3	0.3	0.3	0.3	0.7
di-phenyl <i>p.</i> phenylene dia- mine	5.7	6.4	7.7	11.8	75.0
di- <i>o</i> -cresylol propane	5.4	10.1	19.0	48.0	87.0
2, 6- <i>t</i> -butyl-4-methyl phe- nol	100.0	—	—	—	—

The added antioxidant should, in addition, have no adverse effect upon the properties of the polythene required for the particular application.

The evaluation and comparison of antioxidants is thus carried out using tests related to the desired properties and service conditions. These tests can be grouped under the headings short term tests and long term tests, as follows.

Short term tests: volatility; discolouration on milling into polythene and during subsequent outdoor exposure; "blooming" and "bleeding" tests; short term milling at 145°C.

Long term tests: prolonged milling at 160°C; oxidation in aerated water at 90–95°C; oxidation in air at 105°C.

Comparative figures for a few well-known antioxidants, together with their structural formulae, are quoted in Tables 6.1 and 6.2.

SHORT TERM TESTS

Volatility

While a volatile antioxidant may, in itself, be a good inhibitor of oxidation, its proneness to volatilize during hot processing and in subsequent service renders it less effective in applications requiring long term protection. The value obtained for the volatility is thus a guide to long term performance. As can be seen from the tables di-*t*-butyl *p.* cresol and di-*ortho*-cresylol propane are appreciably more volatile than di- β -naphthyl *p.* phenylene diamine and show correspondingly lower inhibiting action against oxidation in elevated temperature tests.

Discolouration

In certain applications utilizing pigmented compositions, particularly in the cable industry where colour coding is used as a means of identifying conductors, modification of basic shade as the result of antioxidant staining cannot be tolerated and the range of available antioxidants is thus limited to those showing freedom from discolouration. As a result

It has not been possible to use the more efficient diamine type antioxidants in such applications. New antioxidants are, however, now becoming available which show inhibiting power comparable with di- β -naphthyl *p*. phenylene diamine but without the associated marked staining effect.

‘Blooming’ and ‘bleeding’

The phenomena of blooming and bleeding are discussed in Chapter 5. In both cases they are undesirable characteristics for an antioxidant to possess. The migration, either by blooming or bleeding, of an antioxidant from the polythene to either the surface or an adjacent material has, of course, an additional disadvantage of lowering the effective residual concentration within the polythene itself. Diphenyl *p*. phenylene diamine and di-*o*-cresylol propane both show marked bloom at 0.1% concentration, and at the same concentration di- β -naphthyl *p*. phenylene diamine shows evidence of bleeding, as also does diphenyl *p*. phenylene diamine. In the case of the two amine antioxidants the migration effect is particularly undesirable since it is associated with the staining of adjacent materials. Additionally, the residual antioxidant content of the polythene is reduced.

Milling tests on rolls

Hot milling constitutes a rapid means of assessing the inhibiting power, permanence and staining tendency of an antioxidant. Effectiveness is assessed from periodic measurement of power factor and melt viscosity. Good long term antioxidants stabilize these two properties over periods of at least three hours at 160°C.

LONG TERM TESTS

Long term immersion in aerated water at elevated temperatures

This severe test was originally designed to assess the suitability of antioxidants for polythene pipe compositions for hot water services where leaching and oxidation occur simultaneously. Fig. 6.6 illustrates the form of apparatus used for this test. The specimen containing antioxidant is in the form of a power factor disc 30 mils thick, 2 in. diameter. A glass holder supports the sample, and a regulated stream of filtered air is bubbled through the water which is changed regularly. The test temperature is maintained constant by heat transfer from the liquid boiling in the outer vessel. Typical curves are shown in Fig. 6.7.

It will be observed that there is an induction period during which the power factor remains low, the duration of this stage giving a relative measure of the performance of the antioxidant. The power factor subsequently shows a rapid rise indicating the termination of inhibiting action.

Long term oxidation in air at 105°C

Curves similar in form to those shown in Fig. 6.7 are plotted for power factor discs maintained in air at 105°C. In the case of stabilized samples

the leaching action of water is absent and the tests are more prolonged. Compared with a control sample of unstabilized polythene where rapid rise of power factor is very soon observed induction periods of approximately 350 hours and over 5,000 hours are obtained when 0.1% of

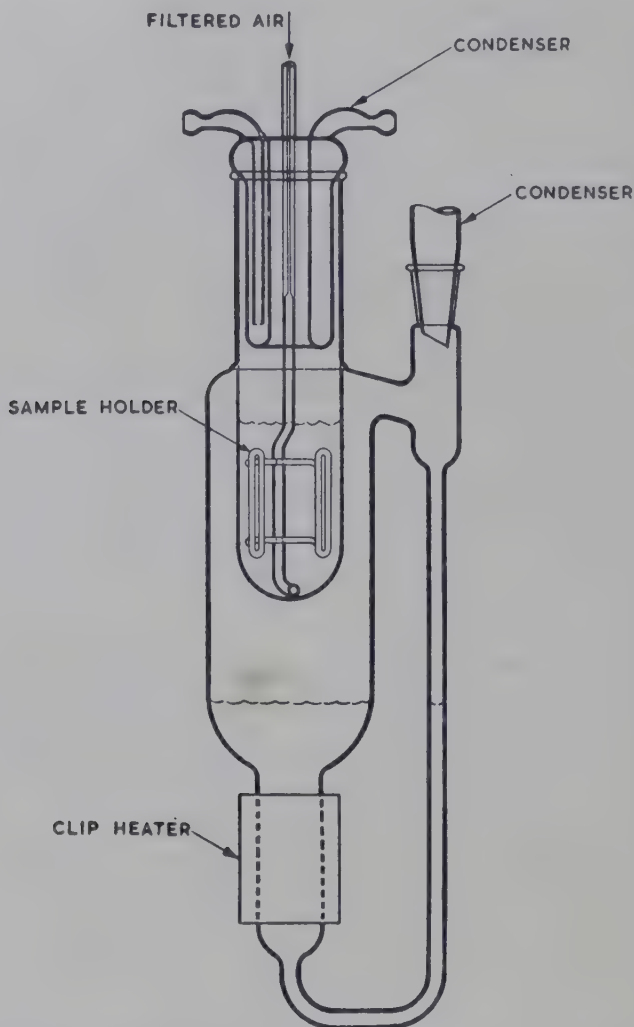


Fig. 6.6. Ageing in aerated water at elevated temperatures. Diagram of apparatus

di-*o*-cresylol propane and di- β -naphthyl *p*. phenylene diamine respectively are present.

The effect of concentration of antioxidant is broadly as would be expected, illustrated in Fig. 6.8 for diphenyl *p*. phenylene diamine.

For the majority of cable applications 0.07–0.10% of antioxidant is used. Concentrations of this order minimise troubles due to incompatibility while still affording a greatly prolonged service life in contrast to unstabilized polythene.

OUTDOOR AGEING

Weathering studies have been carried out in England, India and the U.S. to assess the protective power of light-screening agents for polythene and to obtain information on the useful life which might be expected

OXIDATION AND AGEING

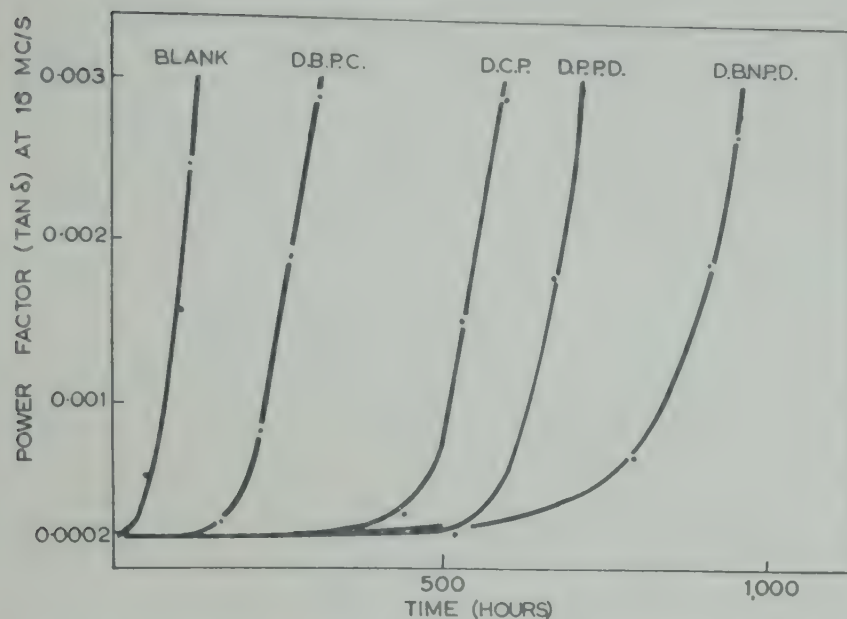


Fig. 6.7. Oxidation of polythene in water at 93°C. Effect of antioxidants at 0.1% concentration. D.B.P.C.—di-*t*-butyl *p*-cresol; D.C.P.—di-*o*-cresylol propane; D.P.P.D.—diphenyl-*p*-phenylene diamine; D.B.N.P.D.—di-β-naphthyl *p*-phenylene diamine.

under specific conditions for suitably protected fabricated sections. Accelerated tests have been used^{12, 13} to help predict the natural ageing performance of compounds, although actual outdoor trials are essential to confirm laboratory experiments. The necessity for this is obvious when one considers the inevitable difference between natural and artificial sunlight, the thermal expansion and contraction and effect of water upon samples exposed outdoors to different climatic conditions.

It has been shown that the flexibility of polythene is most sensitive to

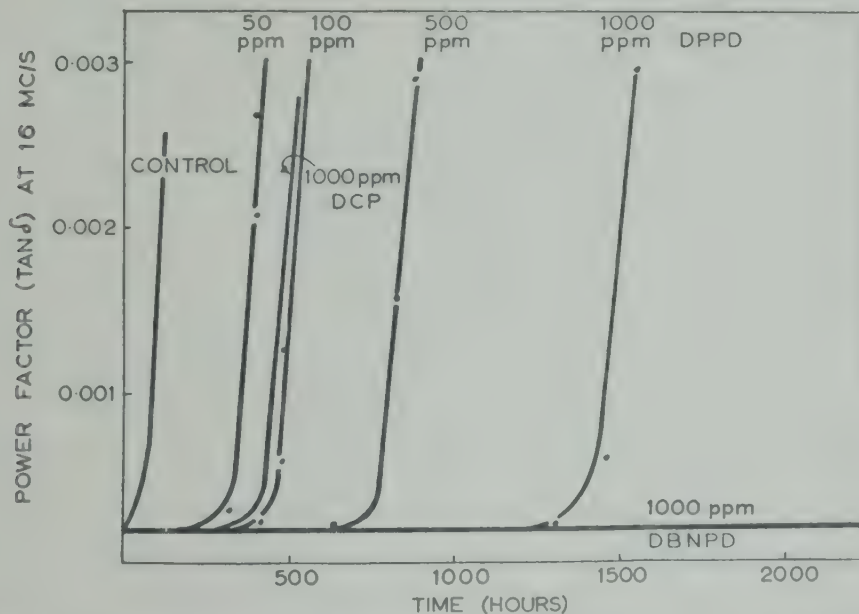


Fig. 6.8. Oxidation of polythene in air at 105°C. Effect of concentration of antioxidant (diphenyl-*p*-phenylene diamine)

change in surface condition of the material and the measurement of brittle point has been largely used to follow the progress of degradation.

Of many pigments and U.V. absorbing compounds examined in polythene, only carbon black of fine particle size has been shown to prolong the life of exposed polythene to any useful extent. Surface coating with aluminium powder, while conferring a marked improvement on weathering life by reflection of light, is not considered practicable for general applications where abrasion of the surface is likely. When dispersed into polythene it has been found of little or no protective value.

Plate 6.1 illustrates the effect of two years exposure in Pakistan upon polythene tube containing 5% well dispersed titanium dioxide. The sample shows extensive surface crazing and brittleness at room temperature.

The factors affecting the weathering life of a carbon black compound are notably: the type of black, and particle size; the concentration of carbon black; the degree of dispersion.

Other factors are the influence of added antioxidant and the effect of residual processing strain. Geographical location and the siting of specimens are also of major importance. In controlled experiments samples have been inclined due South at 45° so as to suffer the most severe exposure. Experiments carried out in India on polythene containing 0.5% carbon black have shown that a particle size of 25 millimicrons or smaller is necessary for maximum protection; the particle size of normal grades of carbon black used is 15 m μ .

Similar tests have indicated that a minimum concentration of 2% is necessary to ensure a life under the most severe conditions of 5 years or more. Compositions exposed in Calcutta containing 0.5% and 1.0% carbon black were found brittle on hand flexing at room temperature after 18 months and 2 years respectively, while a 2% compound remained practically unchanged after 5 years. Artificial ageing tests carried out in the Bell Telephone Laboratories showed no improvement in ageing for a 5% compared with a 2% black compound, though it is likely that some increase in life would be found in practice due to the denser screening action at the higher concentration. In this respect, however, the effect of concentration upon mechanical properties must be taken into account. At 2.0–3.0% carbon black content this is still only slight and such a concentration thus provides an acceptable working compromise.

The dispersion of the carbon black is highly important and care must be taken during processing to ensure that complete dispersion is achieved in the fabricated product. Only in this way, and through the use of very small particle size, can the degrading action of sunlight be restricted to the extreme surface layer. Either black compound is used, or a tumble-blend of concentrated carbon black master-batch and natural granules. In the latter case the extrusion equipment employed must be capable of homogenising and dispersing the black to the necessary extent.

The degree of dispersion achieved is most conveniently checked by microscopic examination of 1 mil specimens at 100–200 magnification

sing strong illumination. The specimens are prepared either by microtoming a thin section or by pressing out a thin film between heated microscope slides. The quality of the dispersion is assessed by comparison with standards. This method is qualitative and is intended to detect the presence of agglomerates and streaky dispersions. Attempts are being made to introduce photoelectric techniques to measure the light-absorbing power of the dispersed black. The main difficulty with such a test however, is the accurate preparation of the test specimens at thicknesses of the order of $\frac{1}{2}$ mil. Under the microscope a good dispersion presents a uniform light-brown background (in which the carbon black is virtually indistinguishable), and which is substantially free from visible agglomerates. A poor dispersion, on the other hand, shows a very light or patchy background with marked evidence of agglomeration. Streaky dispersions are likely to occur where tumble blends of masterbatch and natural granules are extruded on equipment providing insufficient work input to homogenise the blend thoroughly. While the product may appear on cursory examination to be of satisfactory quality, the presence of the surface layer of minute areas of incompletely protected polythene serves to provide centres for the initiation of U.V. degradation on subsequent exposure. As soon as oxidation has occurred at these points they become stress concentration centres for the release of strain induced by mechanical flexing in service.

Once a crack is initiated in the surface it can then propagate rapidly through the underlying layers and so produce extensive physical deterioration. In cable applications this effect can lead to early failure due to moisture penetration and in the case of pipe used for water services to premature bursting under pressure.

Experimental samples of polythene containing 2% carbon black extruded from a tumble-blend under conditions such as to give very streaky dispersion became brittle at room temperature after less than two years' exposure in India.

A similarly exposed specimen, prepared from fully compounded material, continues to survive practically unchanged after 5 years. Plate 6.2 illustrates these two types of dispersion.

The incorporation of an efficient thermal antioxidant, such as di- β -naphthyl *p*. phenylene diamine, into black polythene compounds is desirable to minimise the effect of thermal degradation, particularly in hot climates. In India, for example, the temperature of black polythene exposed to intense sunlight can rise to as much as 55°C, and while thermal oxidation occurs relatively slowly at this temperature evidence from weathering experiments in Calcutta has indicated that under such conditions a significant improvement in service life is to be expected by inclusion in the compound of 0.1–0.2% of antioxidant.

While natural ageing trials are still continuing it is only possible to make tentative estimates of useful life upon the basis of accumulated evidence to date. This suggests it is not unreasonable to expect minimum lives of some 6–10 years under the most severe exposure conditions and

of 20 years upwards in temperate climates for suitably protected polythene.

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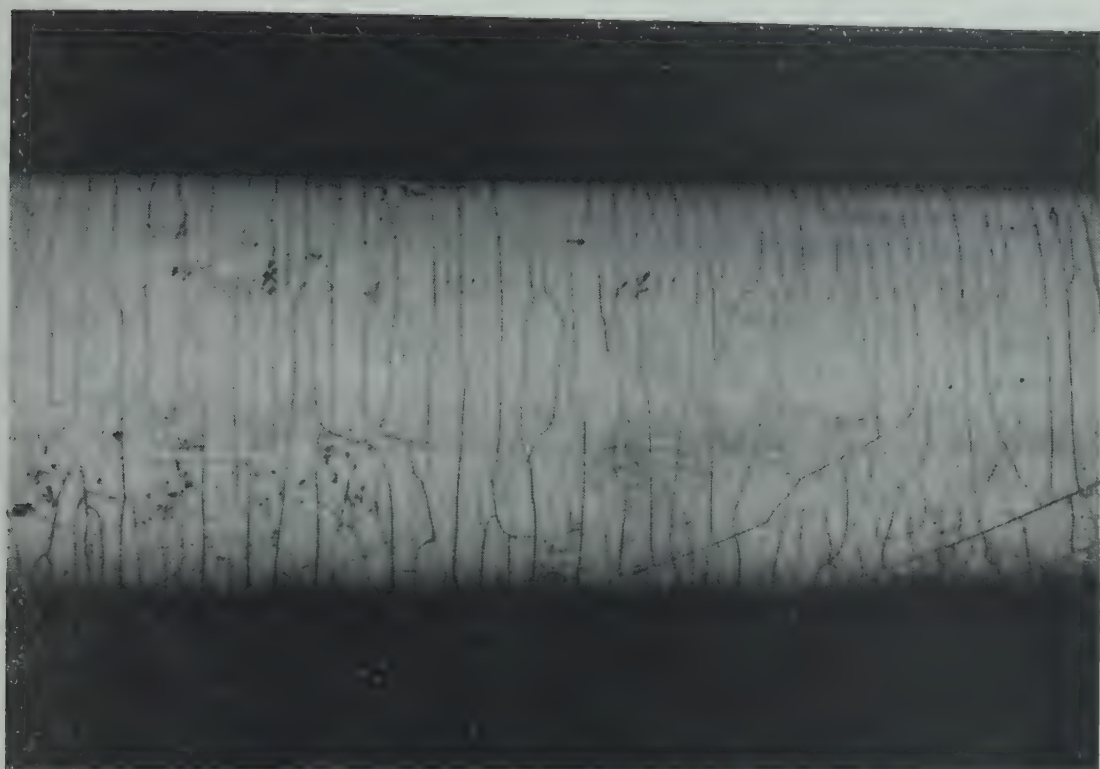


Plate 6.1. Polythene pipe, containing 5% titanium dioxide, shows extensive crazing and brittleness after two years' exposure



Plate 6.2. Top, sample extrusion from tumble blend giving streaky dispersion of 2% carbon black became brittle after two years' exposure in India. Bottom, sample is fully compounded, and after same exposure for five years is practically unchanged

CHAPTER 7

MOLECULAR STRUCTURE

C. W. BUNN

OUR knowledge of the molecular structure of polythene rests almost entirely on evidence derived from physical, as opposed to chemical methods. Chemical analysis tells us little more than that its empirical formula is substantially $(\text{CH}_2)_n$, as we should expect. The only other element present in detectable proportion in polythene made by the high pressure process is oxygen in minute amount, derived from the catalyst; with some difficulty it can be estimated by chemical methods, but infra-red absorption spectrometry is required to establish the manner in which it is linked chemically. Polythenes made by low pressure processes may give very small amounts of ash, in which certain metallic elements (derived from the catalysts) can be detected. The amounts of elements other than carbon and hydrogen are so small that they can have little influence on most of the properties of the polymer, but the electrical properties may be appreciably affected.

STRUCTURE OF THE MOLECULES

Infra-red absorption spectra (see Fig. 7.1) show very strong bands which leave no doubt that the molecules consist for the most part of

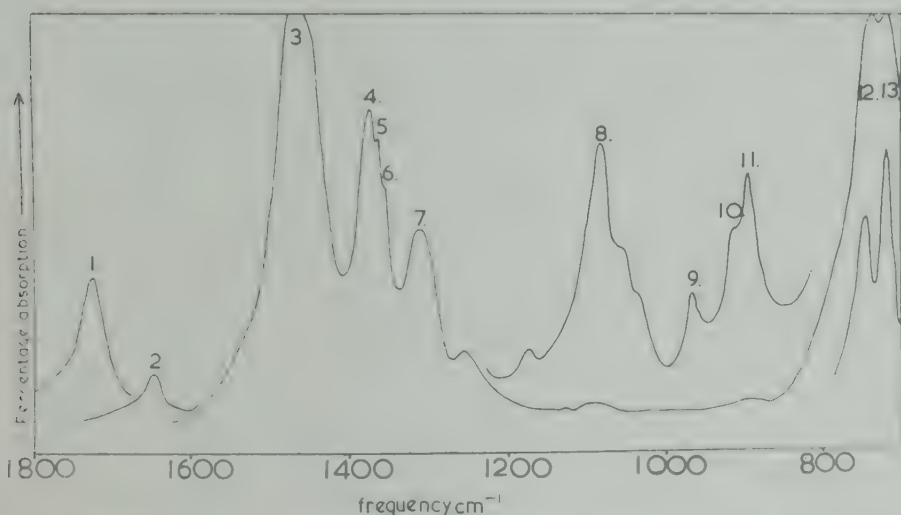


Fig. 7.1. Infra-red absorption spectrum of high pressure polythene. Main spectrum—specimen 4 mils thick; upper, 40 mils; lower, 1 mil. Peaks: 1, $\text{C}=\text{O}$ stretching (oxidized polymer). 2, $\text{C}=\text{C}$ stretching. 3, CH_2 symmetric deformation. 4, CH_3 symmetric deformation. 5 and 6, CH_2 wagging. 7, CH_2 wagging (amorphous). 8, $\text{C}-\text{C}$ stretching. 9–11, CH out-of-plane deformation in $\text{R}_1\text{CH}=\text{CH}\text{R}_2$ (9), in $\text{RCH}=\text{CH}_2$ (10), and in $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$ (11). 12, CH_2 rocking in crystal, polarized along a axis. 13, CH_2 rocking in crystal, polarized along b axis, and in amorphous regions

CH₂ chains: there are the C—H stretching bands of the CH₂ group at 2,850 cm⁻¹ (symmetric stretching) and 2,926 cm⁻¹ (asymmetric stretching), a doublet at 1,464 and 1,473 cm⁻¹ due to symmetric deformation⁶¹, and a doublet at 720 and 730 cm⁻¹ due to asymmetric deformation^{62,63}. Bands at these positions are strong for all molecules consisting largely of CH₂ chains—short chain normal paraffins and polymethylene made from diazomethane¹, as well as polythenes made by both high and low pressure processes. (Note, however, that only crystalline specimens give the doublets mentioned; for liquids the doublets are replaced by single bands). The X-ray diffraction patterns of all these substances are also very closely similar to each other, and atomic positions in the crystalline regions, deduced by detailed interpretation of the diffraction pattern of polythene³⁰, leave no doubt that in the crystalline regions the molecules are simply unbranched CH₂ chains.

The infra-red absorption spectra of most specimens show also bands due to CH₃ groups, notably a symmetric stretching band² at 2,962 cm⁻¹, and a symmetric deformation band³ at 1,378 cm⁻¹. These bands are given by monomeric branched paraffin hydrocarbons with an intensity proportional to the number of chain ends, and they also appear strongly in the spectra of polyethylidene (—CH(CH₃)—)_p and polypropylidene (—CH(C₂H₅)—)_p¹. For low density polythenes the intensities of these bands are much greater than could be accounted for by the ends of unbranched chains; they show that each molecule is branched. The extent of branching varies with polymerization conditions and with molecular weight; on the average there are 50 chain ends per molecule, and a branch point every 40 or 50 carbon atoms along a chain. The variation is discussed later in the section on molecular weight. For high density polythenes these bands are very weak, showing that there is little, if any, branching.

Absorption bands due to various types of unsaturated groups are also found^{6, 7, 23} and the proportions of these groups can be estimated from the intensities; the total number, in I.C.I. low density polythenes of number average molecular weight 20,000, is around one per molecule. Double bonds would be expected at some of the chain ends, and indeed bands at 909, 990, and 1,645 cm⁻¹ due to the group R·CH = CH₂ are found; but in low density polythenes some four-fifths of the unsaturated groups are pendant methylene groups R₁R₂C = CH₂ (bands at 887 and 1,640 cm⁻¹), the remainder being chain unsaturated groups R₁CH = CHR₂ (700 cm⁻¹ *cis*, 964 and 1,660 cm⁻¹ *trans*) and the end groups mentioned, in about equal proportions. Further details are given in Table 7.1.²³

A weak band at 1,720 cm⁻¹ due to C=O stretching is sometimes found; the oxygen presumably comes from oxygen-containing catalysts used in the high-pressure process, or oxygen as impurity in the ethylene. A hydroxyl band at 3,300 cm⁻¹ is also sometimes found. The intensities of both these bands increase when polythene is heated in air. There is no evidence for the presence of oxygen atoms in the chains. Oxidized polythene shows a hydroperoxide band at 1,132 cm⁻¹ at 150°C^{69, 70}

MOLECULAR STRUCTURE

Table 7.1. UNSATURATION IN I.C.I. LOW DENSITY POLYTHENES

Melt flow index	Molecular weight (number average)	Unsaturation in % C atoms linked by double bonds				Double bonds per mole- cule
		$R_1CH=CHR_2$	$RCH=CH_2$	$R_1R_2C=CH_2$	Total	
0.07		0.0022	0.0063	0.033	0.0415	
0.2	(48,000)*	0.0059	0.0056	0.041	0.0525	0.90
0.7		0.0065	0.0067	0.044	0.0572	
2	(32,000)	0.0051	0.0060	0.049	0.0601	0.69
7	(28,000)	0.0056	0.0093	0.084	0.0989	0.99
20	(24,000)	0.0081	0.0107	0.094	0.113	0.97
70	(21,000)	0.0138	0.0177	0.107	0.139	1.04
200	(19,000)	0.0163	0.0198	0.128	0.164	1.11
200,000	3,500	0.038	0.066	0.215	0.319	0.40
700,000	2,000	0.12	0.16	0.50	0.78	0.56

* Figures in brackets do not refer to the same samples as those used for the infra-red data; they refer to different samples of the same melt flow index.

which on cooling is replaced by a band at $1,072\text{ cm}^{-1}$; it has been suggested⁷⁰ that the change is due to association of hydroperoxide groups in the solid state.

From the methods of preparation, we expect any specimen of polythene to contain molecules of a wide range of sizes; it is evident therefore that for an adequate description of the molecular structure, we should need to know not only the proportions of the various chemical groups already enumerated but also the average molecular weight and the distribution of molecular weights. Moreover, we should like to know not only the frequency of the branch points but also the distribution of branch lengths. Since it is these features of the molecular structure—the molecular weight distribution and the branch structure—which appear to control the variations in most of the physical properties, great efforts have been made to develop methods of measuring them. It is very difficult to obtain detailed information, but some progress has been made in recent years, and this will now be described.

Molecular weight and molecular weight distribution

A single measurement made with an unfractionated polymer specimen will of course give some sort of average molecular weight, and different methods give different types of average. The simplest sort of average, the number average, \bar{M}_n is the weight of all the molecules divided by the total number of molecules:

$$\bar{M}_n = \frac{\sum M_i n_i}{\sum n_i}$$

where M_i is the molecular weight of molecules of a certain size i and n_i the number of that size; and it is this type of average that is given by

measurements of the osmotic pressure, the elevation of the boiling point or the depression of the freezing point of a solution, because each molecule makes a contribution independent of its size. For some other solution properties, the contribution of each molecule depends on its size and shape in solution, so that the single value given by any measurement is a more complex function of the distribution of molecular species. One property, the scattering of light by a solution, is unique in depending^{14, 15} on the weight average molecular weight \bar{M}_w which is defined as

$$\frac{\sum M_i w_i}{\sum w_i}$$

where w_i is the total weight of molecules of a given size i . (The overall shape of the molecules in solution, if it is not spherical, influences the scattering of light, but this influence is revealed by an angular dissymetry of scattered light (difference between scattering at θ and $180^\circ - \theta$) and a correction can be applied).

The results of measurements of these two sorts of average for the same heterogeneous specimen will not be the same, for a small proportion of small molecules have a large effect in reducing the number average molecular weight, while the large molecules have a greater effect on the weight average molecular weight. It follows that the ratio of these two sorts of average gives some idea of the range of molecular sizes in the specimen; the determination of this ratio has been much used in seeking information on molecular weight distribution. More detailed information could of course be obtained if the specimen could be separated into fractions of sharply defined molecular weight; this has been attempted, but it is difficult and laborious, and the fractions are far from sharp.

Number average molecular weight measurements have been made by many workers, and values varying from 2,000–5,000 for waxy and greasy materials to 20,000–40,000 for the more important commercial materials cover the vast majority of samples. The freezing point and boiling point methods are suitable only for the lower end of this range. For molecular weights up to about 4,000 cryoscopy has been used by Ueberreiter and his collaborators⁸. Ebulliometry is now regarded as reliable up to values of about 20,000⁹, although it can, under special circumstances, be used for higher molecular weights, as Ray¹⁰ has shown. But the majority of samples have been studied by osmometry, and in this field Harris¹¹ reports values of 18,000–76,000, Muthana and Mark¹² 10,000–37,000, Ueberreiter *et al*⁸ 18,000–45,000, and McCrae¹³ 20,000–40,000. These results merely tell us that if polythene is described simply as $(\text{CH}_2)_n$, then the number average value of n ranges from about 150 to 6,000 if we include the extreme samples, but for the most important commercial materials it lies in the range 1,500 to 3,000.

Because each method is peculiarly suited to its own range of molecular weights, there are few results available which enable the results of one method to be compared with those of another. The results in Table 7.2, however, show that in the region of 20,000 the results of ebulliometric

Table 7.2. COMPARISON OF OSMOMETRIC AND EBULLIOMETRIC NUMBER
AVERAGE MOLECULAR WEIGHTS OF POLYTHENE

Osmometric molecular weight ¹³	Ebulliometric molecular weight ⁹		
	In toluene	In carbon tetra- chloride	In <i>n</i> -octane
	2,840	2,840	2,840
	4,230	4,680	
7,000	4,000	4,500	
	5,260	5,940	6,610
10,000	7,090		
15,000	7,670	8,940	9,360
14,000	12,700	16,500	
16,000	13,000	17,280	
19,000	16,100	20,700	18,700
25,000	17,400	31,400	

and osmometric measurements agree quite reasonably. Below this figure osmometry, probably because of diffusion, gives higher values than ebulliometry.

The only published data on the weight average molecular weight of polythene as measured by the light scattering method first developed by Debye^{14, 15} appear to be those of Billmeyer¹⁶ who reports values of M_w (in low density polythenes) varying from 43,000 to 1,800,000 and values of M_w/M_n varying from 1.9 to over 40. These figures demonstrate that polythene may contain a very wide range of molecular weights. Billmeyer's figures for M_w (and therefore for M_w/M_n) are likely to be lower than their true values because he applied a theoretical correction for the angular dissymmetry of scatter which, in the light of recent measurements by D. J. Smith and H. Smith¹⁷, would appear to be too small. Despite this the results of D. J. Smith and H. Smith¹⁷ (M_w from 50,000 to 1,000,000 and M_w/M_n as high as 20 in some cases) broadly confirm Billmeyer's results.

The results of attempts at fractionation suggest a narrower molecular weight distribution. Thus Bebbington, Hunter, and Richards²⁰ report values of M_w/M_n in the range 2-3 and the work of Ueberreiter et al,⁸ Desreux and Spiegels²¹ and McCrae¹³ also gives no evidence of broad molecular weight distributions. There is now, however, considerable evidence to show that the fractionation method of Desreux and Spiegels, which involves the solution-extraction of polythene at successively increasing temperatures, does not yield sharp fractions; and furthermore, that structural factors, in addition to molecular weight, are important in determining the solubility characteristics of polythene. Desreux and Spiegels themselves found that the intrinsic viscosity of their fractions did not always increase regularly with increasing temperature of extraction. McCrae's results for fractions obtained by the Desreux and Spiegels method show that the molecular weight can vary irregularly with the

temperature of extraction; these are shown in Table 7.3, where the figures for tensile strength and melt flow index are also given. It will be noted that these two properties tend to run parallel to the molecular weights of the fractions.

McCrae's¹³ number average molecular weights and the light-scattering results of D. J. Smith and H. Smith¹⁷ show that the extraction method yields fractions which are far from being sharp; the \bar{M}_w/\bar{M}_n values for the higher molecular weight fractions in particular are large and often exceed that for the parent polymer.

Baskett¹⁹ has fractionated polymethylene by the method of Desreux and Spiegels, and has shown that it is extracted at temperatures between 100°C and 110°C. His collected data for many samples of polythene are shown in Fig. 7.2, in which the number of methyl groups per 100 carbon atoms (determined by the infra-red method) is plotted against temperature of extraction. The correlation between the two properties is obvious, and if we accept the number of methyl groups per 100 carbon atoms as a measure of the degree of branching, then the fact that the point for polymethylene (for which this number is near zero) lies on the curve strongly suggests that the solubility characteristics of polythene depend on the degree of branching as well as on the molecular weight. The results of solvent fractionation experiments therefore do not give reliable information about the molecular weight distribution.

The development of a valuable method of estimating the molecular weight distribution has resulted from the discovery of the effects of high-energy radiation on polythene. Charlesby⁹⁹ found that the main effect is that the molecules become cross-linked, presumably in a random manner, and, as a result of a sufficient degree of crosslinking, an insoluble gel is formed. The way in which the proportion of insoluble gel formed increases with the degree of random cross-linking depends on the molecular weight distribution in the original material,¹⁰⁰ and Baskett¹⁰¹ has

Table 7.3. PROPERTIES OF FRACTIONS OBTAINED BY THE DESREUX AND SPIEGELS METHOD

Temperature of extraction (°C)	Melt flow index	Tensile strength (kg/sq.cm)	\bar{M}_n
Up to 57°			5,000
57-62.7	139	114	16,000
62.7-64.4	18.4	107	25,000
64.4-66.0	2.7	174	35,000
66.0-67.0	1.37	173	42,000
67.0-67.5	2.12	167	36,000
67.5-68.5	2.10	143	35,000
68.5-68.9	0.46	177	49,000
68.9-69.3	0.42	180	51,000
69.3-69.7		180	53,000
69.7-70.5	0.25	168	50,000
70.5-71.0	0.12	191	51,000
71.0-72.0	0.20	193	53,000

MOLECULAR STRUCTURE

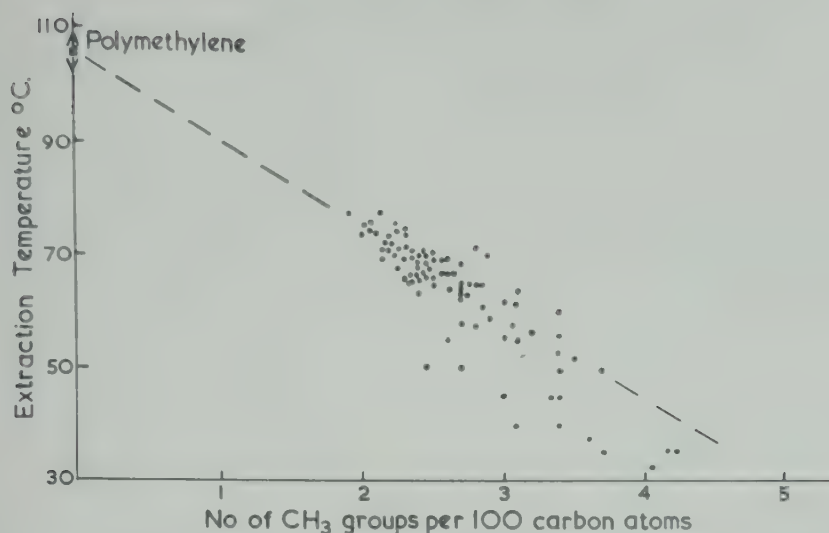


Fig. 7.2. Temperature of extraction by solvent, in relation to branching of molecules

developed a mathematical treatment which gives expressions of such a form that the original molecular weight distribution can be calculated from the proportions of soluble and insoluble material in a series of samples of the same material irradiated for different lengths of time. (The number of cross-links per unit of radiation has been established by Charlesby).¹⁰⁵ In addition to cross-linking, a certain amount of chain

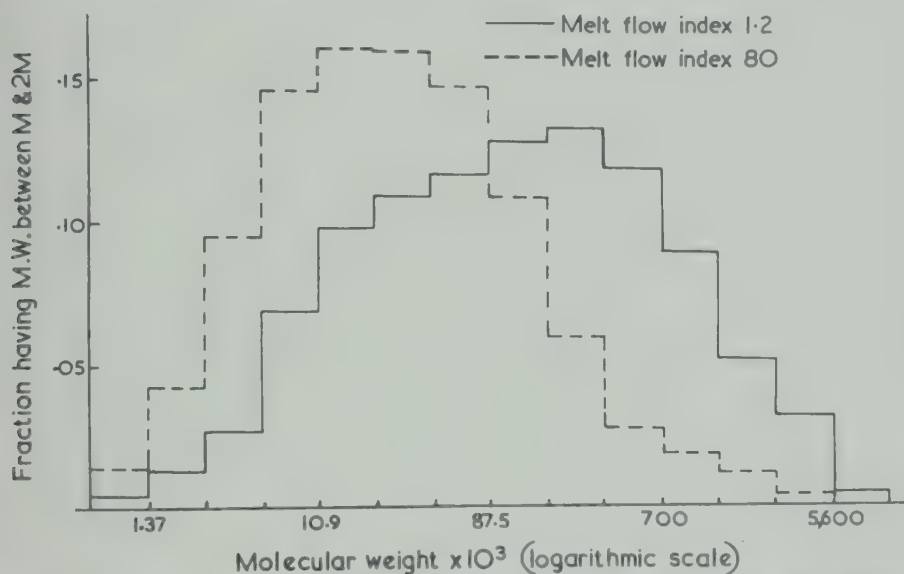


Fig. 7.3. Molecular weight distribution in two polythenes, calculated from proportions of soluble and insoluble material in series of irradiated samples

scission occurs,¹⁰² and it is necessary to estimate this¹⁸ and correct for it.¹⁰¹ In Baskett's experiments, the polythene was irradiated with high energy electrons from a travelling wave linear accelerator; soluble material was extracted with toluene at 100°C.

The results of such experiments are illustrated in Fig. 7.3, which shows the molecular weight distribution in two specimens of polythene having

melt flow indexes of 1.2 and 80. The distribution is very broad in both of these, and in a number of other specimens which were examined; the ratio of weight average to number average molecular weight calculated from these results ranges from 5 to 20; the indications of a very broad molecular weight distribution given by the earlier light-scattering work are thus confirmed. The distribution is, in fact, similar to that given by Beasley's theory²⁸ for a polymerization mechanism in which the termination of a growing polymer chain by transfer with dead polymer plays an important part; termination in this way would give molecules with long branches.

Chain branching in polythene

Since the branches of a polythene molecule are presumably terminated by either methyl ($-\text{CH}_3$) or vinyl ($-\text{CH}=\text{CH}_2$) groups, and since the latter are present in very small numbers, the former will largely determine the total number of branches. The quantitative determination of the methyl content of polythene can be carried out by the infra-red methods described by Cross, Richards, and Willis,²² based on the intensities of the absorption bands at 1,378 and 891 cm^{-1} ; it is advisable to do this with a spectrometer of high resolving power, to separate the methyl bands from neighbouring bands due to other groups. The results in Table 7.4 show that the methyl group content in low density polythene is far in excess of the terminal requirement of one or two per molecule. These results also show that although the number of methyl groups per molecule increases with increasing molecular weight, the degree of branching (expressed by the number of methyl groups per 100 carbon atoms) decreases in this series branching is more frequent in the smaller molecules.

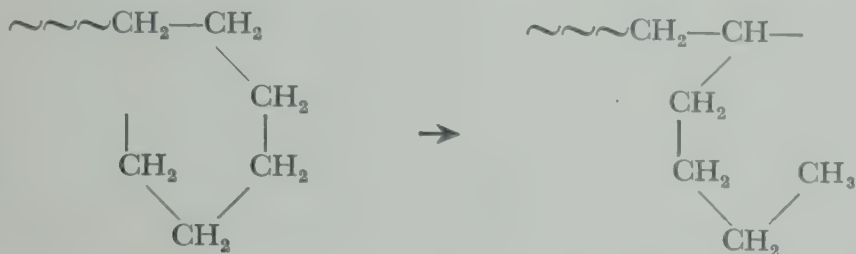
There is little direct experimental evidence regarding the length of the branches. There is a weak infra-red absorption band at 891–894 cm^{-1} which Downing⁴ has assigned to ethyl; on this basis Bryant and Voter⁵

Table 7.4. METHYL GROUP CONTENT OF I.C.I. LOW DENSITY POLYTHENE⁽²³⁾

Melt flow index	Molecular weight M_n	CH_3 groups per 100 carbon atoms	CH_3 groups per molecule
110,000	1,700	4.8	5.5
35,000	2,400	4.4	7.1
11,000	4,000	4.2	11.4
3,200	5,300	4.0	14.5
1,800	6,600	3.8	17.5
170	19,000	3.7	48.5
	21,000	3.3	48.5
20.9	24,000	3.1	52.0
6.4	28,000	2.8	54.0
1.8	32,000	2.3	52.0
0.25	48,000	2.0	67.2
0.005	53,000	1.8	67.5
0.001	76,000	1.8	93.5

report that the ethyl group concentration always runs parallel to the methyl group concentration in different samples, and this would suggest that no simple methyl groups are present. Interpretation of this band is difficult as there is a pendant methylene absorption at the same frequency; this suggestion must therefore be regarded with some reserve.

Roedel²⁶ has suggested that during polymerization an intramolecular hydrogen transfer may take place by a "back-biting" mechanism involving transient rings:



Since five- and six-membered rings are the most likely to be formed, branches four or five carbon atoms long would result. If this is the principal mechanism of branching during the polymerization of ethylene, then most of the branches would be expected to be short. An attempt to estimate the proportion of long branches which has been made by Billmeyer¹⁶ gives some support to this suggestion, if the assumptions involved in the attempt are justified, for he concludes that the number of long branches per molecule is small. His method is based on the consideration that a molecule with long branches will give a lower intrinsic viscosity than an unbranched molecule of the same molecular weight, and in order to convert intrinsic viscosity measurements to what he terms "long chain branching indices" Billmeyer used the calculations of Zimm and Stockmayer²⁷. He measured the weight average molecular weights and intrinsic viscosities of the polythene samples, but for unbranched molecules (i.e. polymethylene) the intrinsic viscosity was not measured but calculated by a method involving the following two assumptions:

- (a) that the relation between intrinsic viscosity and molecular weight given by Harris¹¹ for polythene, i.e.

$$[\eta] = 1.35 \times 10^{-3} [\bar{M}_n]^{0.63}$$

also applies to polymethylene.

- (b) that \bar{M}_w/\bar{M}_n for polymethylene is always 2.

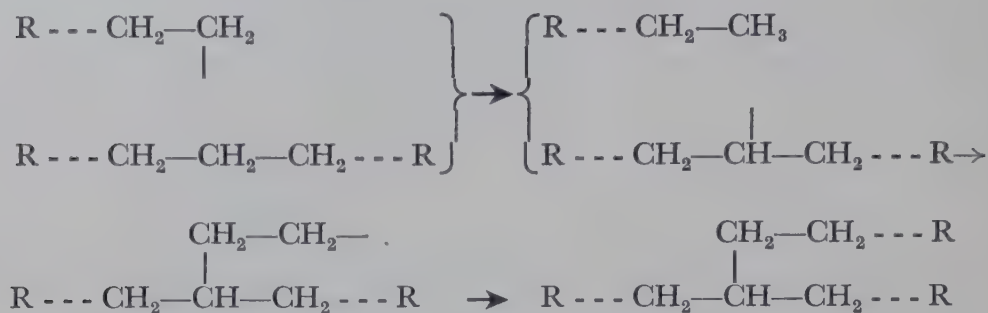
These two assumptions are combined in the expression

$$[\eta] = 8 \times 10^{-4} [\bar{M}_w]^{0.63}$$

so that it is possible to calculate the intrinsic viscosity of a polymethylene of given molecular weight. On the basis of these considerations Billmeyer finds that polythene has a relatively small number of long chain branches, 8-10 per molecule on a weight-average basis. As Roedel²⁶

points out, this is probably equivalent to less than one per molecule on a number-average basis.

Long branches could be produced by termination of a growing chain by hydrogen transfer from dead polymer, which thereby becomes re-activated and grows a long branch:



Beasley²⁸ has calculated the effect of this reaction on molecular weight distribution and shows that the distribution would become very broad. This is consistent with the results of Billmeyer's work which shows that those samples having broader molecular weight distributions do have larger long chain branching indices. It is also consistent with Baskett's molecular weight distributions¹⁰¹, which are of the form required by this theory. The conception of the molecular structure of a typical low density polythene molecule to which these considerations lead thus consists of a chain structure comprising some thousands of carbon atoms, with few long branches but frequent short branches, on the average one every 50 main chain atoms. The considerations leading to this conception are rather speculative. More direct evidence is badly needed; it is very difficult to find.

One surprising feature of the solution behaviour of polythene is the marked correlation (see e.g. Harris¹¹) between the intrinsic viscosity and the number average molecular weight. Specific viscosities are normally regarded as additive upon a weight basis; and for a sample consisting of a mixture of homologues, close though not perfect correlation would be expected between intrinsic viscosity and weight average molecular weight; for samples of variable distribution little or no correlation with number average molecular weight is to be expected. Billmeyer has, however, offered an explanation for the peculiar behaviour of commercial polythene samples in the following terms:

"The intrinsic viscosity of a polythene solution has been found in some cases to be a rough measure of its number average molecular weight. This unusual relationship is the coincidental result of the simultaneous increase in weight average molecular weight due to the branching reaction, and the reduction in intrinsic viscosity from that of linear homologues due to the presence of branched molecules":

When attempts are made to explain the solution and melt properties of polythene in terms of molecular weight and chain branching, a somewhat over-simplified picture may be obtained if these factors cover a

very wide range. As examples of this, the relation between solution viscosity and number average molecular weight observed by Harris¹¹, that between melt viscosity and number average molecular weight observed by Sperati, Franta, and Starkweather²⁵ and by Miller and Small²⁹, and the many other broad correlations reported by Sperati, Franta, and Starkweather may be quoted. The over-simplification arises from the circumstance that very large variations in one of the two variables (molecular weight and chain branching) tend to mask the effect of the other. This is an important aspect of the polythene structure question because the problem most frequently presenting itself is the elucidation of the structure of commercial samples whose properties very often cover only a relatively narrow range.

Many properties of the solid are closely correlated with the degree of branching, because this largely controls the degree of crystallinity. Richards²⁴, observing that the crystallinity decreases with increasing branching, concludes that branch points destroy the crystalline structure in their vicinity. The density, melting point, Young's modulus in tension, yield point, and surface hardness, are very sensitive to degree of crystallinity and thus to the degree of chain branching. Richards points out that the mechanical properties mentioned are characterized by small relative displacements in the solid and hence would be expected to be crystallinity-dependent. Similar conclusions have been reached by Sperati, Franta, and Starkweather²⁵, who also observe that the properties of polythene most sensitive to long chain branching are those associated with its elasticity in the molten state.

Properties which depend on large deformations depend more on the molecular weight than on the crystallinity and the branch structure; properties of this sort are the ultimate tensile strength, the elongation at fracture, and the low temperature brittle point. It is perhaps fair to say that these properties depend on the degree of entanglement of the long chain molecules, and in particular on long-range entanglement, which is obviously increased by rise of molecular weight. The mechanical properties are dealt with in detail in Chapter 9.

Polythenes made by low-pressure processes are little, if at all, branched, and their properties therefore lie at one end of the range covered by high-pressure polythenes. Their densities are in the range 0.94 to 0.96 (high-pressure polythenes range down to 0.90) and their melting points are 125–131°C,⁴⁴ some 15–20° higher than those of low density specimens. The properties of high density polythenes lie, in fact, between those of low density products and those of polymethylene made by polymerization of diazomethane, which melts at 136.5°C, and has a maximum density of 0.98.

TWO-PHASE TEXTURE

X-ray diffraction patterns of low density polythene specimens at room temperature (see Plate 7.1) show numerous fairly sharp diffraction rings, indicating that the molecules are arranged, in at any rate part of the

material, in a precise three-dimensional pattern like that found in crystalline solids generally; in other words, we must imagine the chain molecules packed, locally at any rate, in an orderly manner. The X-ray diffraction photographs show also a pattern of diffuse scattering with a well-marked maximum similar to that given by liquid paraffin hydrocarbons, indicating that not all of the material is crystalline, but that in part of it the molecules are disposed in the irregular manner found in liquids and glasses.

Infra-red absorption spectra give similar evidence: some of the bands correspond to those given only by crystalline paraffin hydrocarbons, others correspond to those given only by these substances in the liquid state. An adequate description of the molecular texture of a polythene specimen would include information on the proportions of crystalline and amorphous material, the sizes of crystalline and amorphous regions and the way in which they are arranged, and the detailed structure of each and its relation to the chemical structure of the molecules.

The X-ray diffraction rings from the crystals are less sharp than those given by large perfect crystals of monomeric substances; such broadening may be due either to small crystal size or to disorder in the crystalline regions. A combination of X-ray, optical, and electron microscopic evidence, which will be discussed in a later section, suggests that the crystalline regions extend for not more than a few hundred Angstrom units in the chain direction, but probably for much greater distances, though with distortion and branching, in a lateral direction. Whole molecules contain thousands of carbon atoms, and unless closely folded up on themselves would extend over much greater distances than the few hundred Angstrom units (or in some specimens less than 100) found for the chain direction; it is most unlikely that very long or very branched molecules would be able to disengage themselves from the vast molecular tangle in a melted specimen, and we suppose therefore that any one molecule participates in a number of crystalline regions, each composed of pieces of a number of different molecules. The parts of the molecules linking the crystalline regions together constitute the amorphous phase. The crystalline and amorphous phases are thus woven together by molecules running through both. This type of structure occurs in crystalline polymers generally (whether the chains are branched or not), and presumably arises in the following way: small pieces of neighbouring chains pack together in a regular way (with the chains straight and parallel) to form crystal nuclei, which then grow, partly by progressive straightening of further lengths of the same chains but mainly by accretion of pieces of other chains. Growth of each crystal proceeds as far as the molecular tangle allows, and the size of a few hundred Angstrom units in the chain direction, which is found not only in polythene but in most crystalline polymers, may represent the limit set by the initial tangle: all molecular chain tangles, whatever the chemical structure of molecules, are somewhat similar in this respect, and would be expected to permit a similar crystal size. A sketch of the sort of structure envisaged is given

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in Fig. 7.4; it takes account also of the spherulitic structure which is discussed later on.

Crystallization is never complete, even in polymers consisting of unbranched chains (such as polymethylene made from diazomethane): if two or more pieces of the same molecule become included in different crystalline regions, intermediate pieces of the same molecule are bound to remain uncrystallized. In low density polythene the proportion of crystalline material is less than in polymethylene: the branch points would not be expected to fit into the crystal structure of the CH_2 chains, and the fact that the proportion of amorphous material increases with

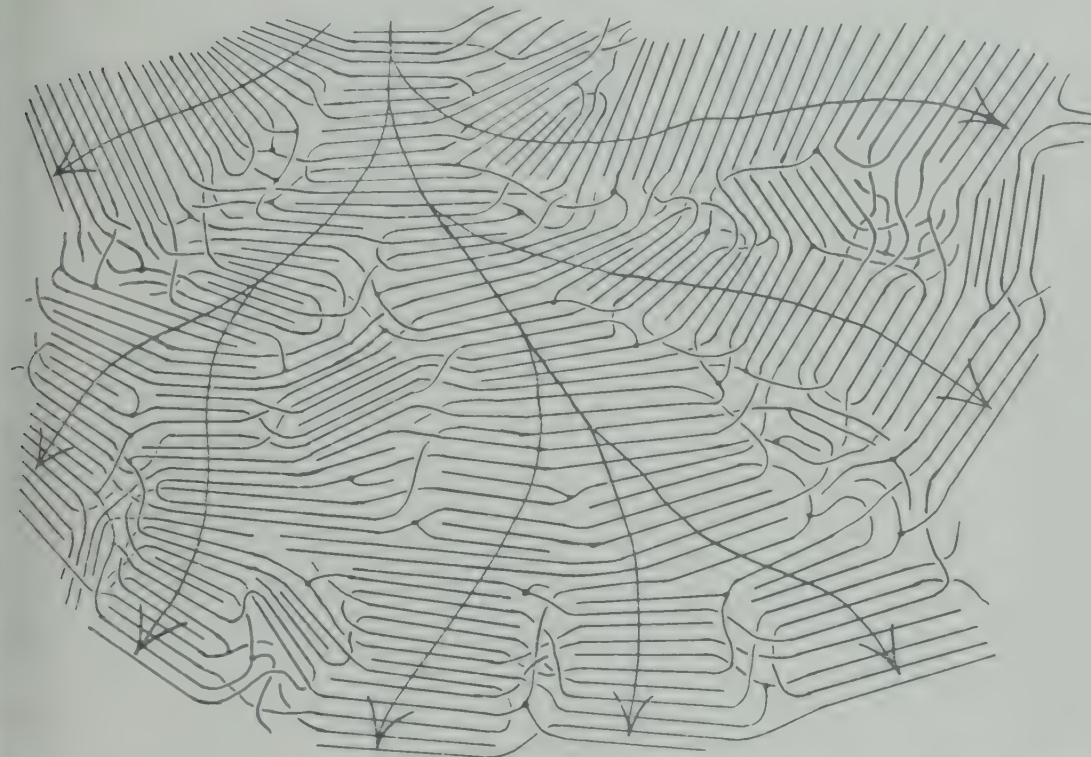


Fig. 7.4. An attempt to depict (as far as this is possible in two dimensions) the molecular arrangement believed to exist in polythene specimens. Regions where molecular segments are straight and parallel are crystalline; other regions are amorphous. Radial crystal growth (suggested by arrows) leads to the formation of spherulites. Compare Plate 7.2

the degree of chain branching (see below) is consistent with this idea. The branch points would also be expected to limit the size of the crystalline regions as well as to reduce the proportion of crystalline material, and it is in general true that the size of the crystalline regions in low density polythene (as indicated by the breadths of X-ray diffraction rings) is smaller for more highly branched specimens.

Structure of crystalline regions

The configuration of the molecules and the exact arrangement of them in the crystalline regions has been found³⁰ by detailed interpretation of the positions and intensities of the diffracted X-ray beams, use being

POLYTHENE

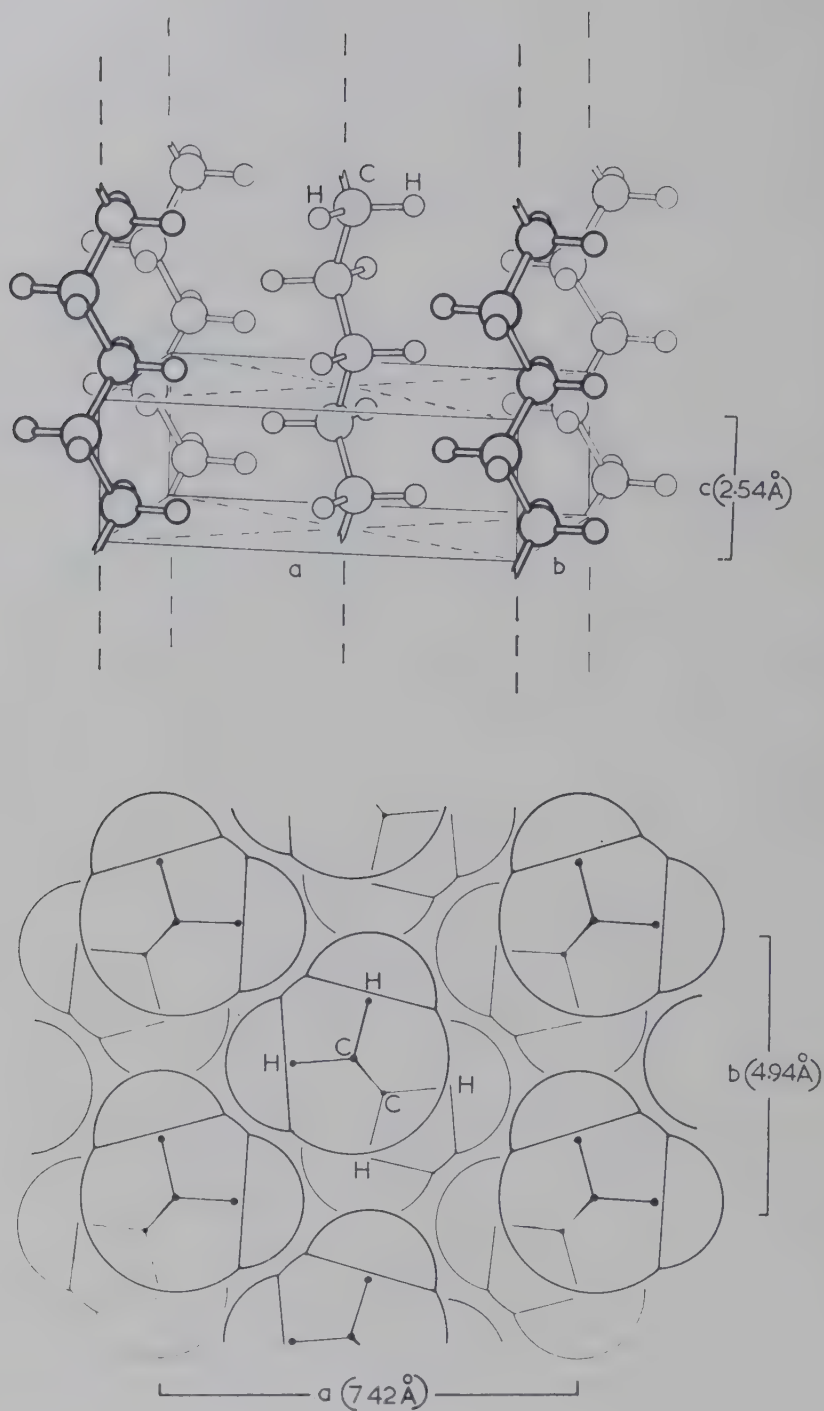


Fig. 7.5. Structure of crystalline regions. Above—general view (the sizes of the spheres representing atoms have no significance); below—view along c axis, showing packing (atoms have correct external radii)

made of drawn and rolled specimens in which the crystals are preferentially oriented and so give X-ray patterns (Plate 7.1) which are more readily and unambiguously interpreted than those of unoriented specimens. The CH_2 chains have the same configuration and are packed side-by-side in the same manner as in the most common crystal structure of the shorter-chained normal paraffin hydrocarbons such as $\text{C}_{36}\text{H}_{74}$ ³¹ and $\text{C}_{60}\text{H}_{122}$.³² The carbon atoms of each chain are linked in the form of a plane zigzag in which the distance between atom centres is 1.53 Å and the angle between the bonds 112°. The chains are packed side by side so that their long axes are parallel, but the zigzag planes are not all parallel—there are two orientations with the zigzag planes at 82° to each other (see Fig. 7.5), the whole arrangement having the orthorhombic space-group symmetry $Pn\bar{a}m$. The dimensions of the rectangular unit cell are:

$$a = 7.42 \text{ Å}, b = 4.94 \text{ Å}, c \text{ (chain axis)} = 2.540 \text{ Å}.$$

(These figures, which apply to unbranched polymethylene as well as to most low density polythenes, are 0.2% higher than those given in ref. 30, owing to a revision of X-ray wavelengths since the paper was published.) The length of the c axis is the span of one zigzag of the chain. The four carbon atoms in the unit cell have their centres at $x, -y, \frac{1}{4}$; $-x, y, \frac{3}{4}$; $-x + \frac{1}{2}, -y + \frac{1}{2}, \frac{3}{4}$; $x + \frac{1}{2}, y + \frac{1}{2}, \frac{1}{4}$, where $x = 0.038a$ and $y = 0.065b$. The positions of hydrogen atoms have not been determined directly from X-ray diffraction data, but their positions may be inferred by assuming a tetrahedral bond configuration and a C—H distance of 1.08 Å. The arrangement of the molecules seems to be determined by their effective shape; carbon and hydrogen atoms behave as spheres with Van der Waals radii of 1.70 Å and 1.25 Å respectively, and neighbouring molecules fit in with each other so that these spheres are just in contact. The relative intensities of the X-ray diffractions show that displacements of the atoms from their mean positions by thermal vibrations and crystal distortions are (as would be expected) much greater in lateral directions than along the chains.

The existence of two different molecular orientations in the crystal is responsible for the splitting of certain infra-red absorption bands into doublets. The phenomenon has been clarified by studies of single crystals of short-chain hydrocarbons with polarized infra-red radiation; it has been shown⁶³ that the band at 730 cm^{-1} is completely polarized along the a axis, while that at 720 cm^{-1} is completely polarized along the b axis of the crystal; the polarization and the difference of frequency are due to coupling of the C—H vibrations of the neighbouring, differently oriented molecules, the "in-phase" deformations giving the higher frequency 730 cm^{-1} and the polarization along a , while the "out-of-phase" deformations give the lower frequency 720 cm^{-1} and the polarization along b ^{63, 93}. For crystals of the short-chain hydrocarbons, these two bands, which are of equal intensity, are replaced on

melting by a single band at 720 cm^{-1} ; for crystalline polythene specimens, the band at 720 cm^{-1} is stronger than that at 730 cm^{-1} , owing to the presence of amorphous material which, like liquid, gives only the 720 cm^{-1} band; on melting, again the band at 730 cm^{-1} disappears. The doublet at $1,464$ and $1,473\text{ cm}^{-1}$ is due to similar effects and behaves in a similar manner.

The density of the crystalline regions, calculated from the unit cell dimensions, is 1.000 at room temperature; the measured densities of specimens are considerably lower (0.90 – 0.96) owing to the presence of less dense amorphous material. With rise of temperature, only the a axis of the unit cell expands appreciably, its length reaching 7.65 \AA at 100°C^{33} . The c axis, being the chain direction, would not be expected to expand, but the approximate constancy of length of the b axis is more surprising. The difference in behaviour of the a and b axes should not be taken as evidence of any difference between the cohesive forces or the amplitudes of thermal motion in the two directions: the change in axial ratio $a : b$ might be brought about by a twist of the mean plane of the zigzag carbon chain towards the ac plane of the unit cell, and is perhaps associated with an increase of amplitude of rotatory oscillations of the molecules, which would cause the packing of the chains to approach a hexagonal arrangement ($a = \sqrt{3} b$) with rise of temperature; this would involve an increase of a relative to b . In some of the shorter-chain paraffins (C_{21} to C_{27}), a hexagonal packing is attained at a first-order transition a few degrees below their melting points, but such a transition has not been detected in polythene³³, for even at temperatures near the melting point a is still very appreciably less than $\sqrt{3} b$.

Small changes in lattice dimensions have been detected in certain polythene specimens; whether these are due to the incorporation of groups other than CH_2 into the crystalline regions, or to strain effects originating in the crystalline-amorphous texture, it is impossible to say. It is known that $\text{C}=\text{O}$ groups can replace CH_2 groups in the crystals, for ethylene-carbon monoxide copolymers crystallize well³⁴. Whether methyl groups (the shortest branch groups) can be incorporated is more debatable; it has been found that in polymeric hydrocarbons deliberately containing methyl groups (made from mixtures of diazomethane and diazoethane¹, the amount of amorphous material increases with the proportion of methyl groups, but at the same time the diffraction pattern of the crystals changes slightly, the a axis (the only one appreciably affected) lengthening to 7.60 \AA (at room temperature). Evidently many of the chain sections containing methyl groups are in the amorphous regions, but the lengthening of the a axis of the crystals may be interpreted as meaning either that an occasional methyl group can be tolerated inside a crystal (though it must cause gross local distortion) or that the very small crystalline regions composed of unbranched chain segments suffer unusually large strains originating at boundaries where side methyl groups bring the regular structure to an end. It should also be remembered that the interpretation of the structure as a clear-cut two-

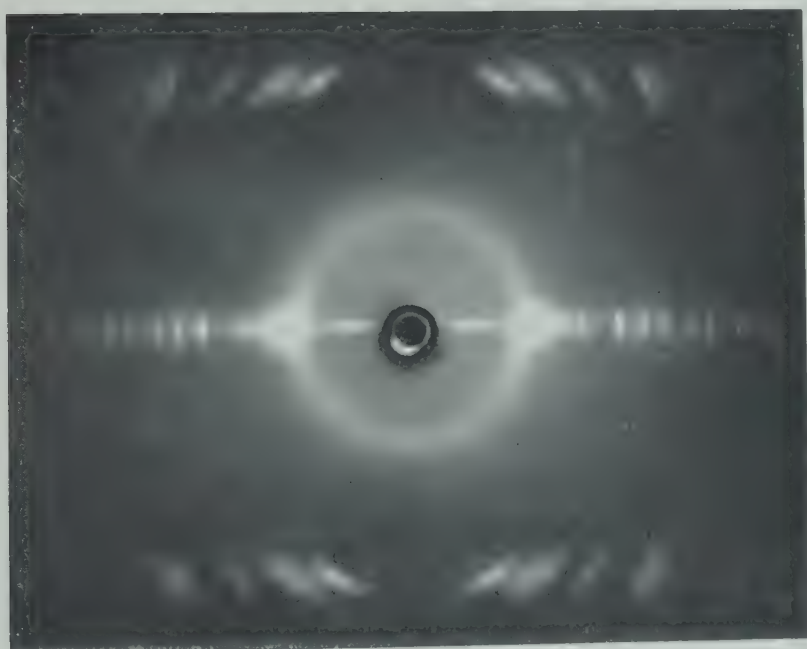
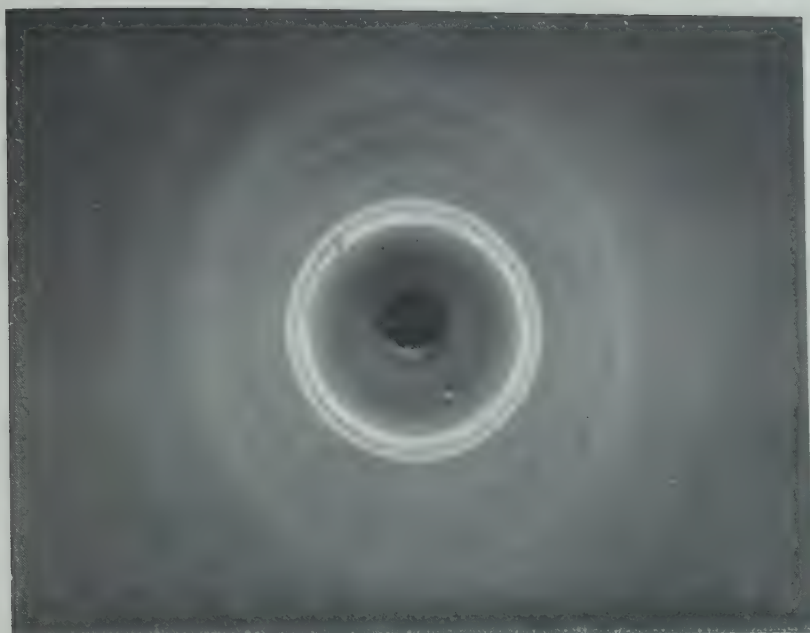
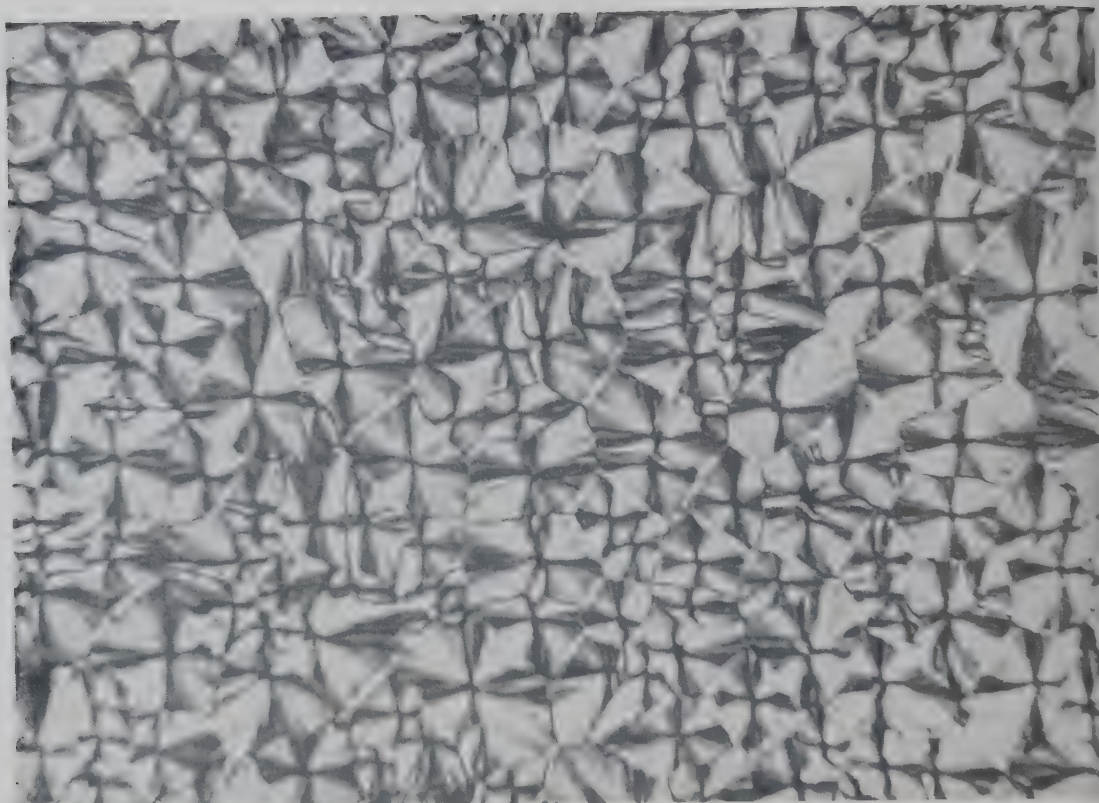


Plate 7.1. X-ray diffraction photographs. Above, unoriented specimen; below, drawn fibre (fibre axis vertical)



*Plate 7.2. Above—thin film of polythene, in optical microscope between crossed polarizers, $\times 600$
(Photograph by R. P. Palmer)*

Below—very thin film, in electron microscope, $\times 10,000$ (Photograph by A. J. Cobbold)

base system is an over-simplification; there are regions in which the degree of order is intermediate between the crystalline and the amorphous, and ideally we should like to express the structure as a distribution of degrees of order; there is, however, too little experimental evidence for this to be possible, and the best that can be done at present with either X-ray diffraction patterns or infra-red absorption spectra is to interpret them as if the specimens were clear-cut mixtures of crystalline and amorphous regions, while realizing that this is an undue simplification.

In X-ray diffraction patterns of polythenes, additional crystal diffractions are sometimes seen which do not fit the normal crystal structure; they are sometimes very much strengthened in cold-worked specimens (for instance, in film re-drawn³⁵ or re-rolled³¹ several times, alternately in two mutually perpendicular directions). They are probably due to a second type of crystal structure in which the CH_2 chains are packed in a different way from that found in the normal structure. It is known that some of the shorter-chain hydrocarbons can form alternative molecular arrangements of monoclinic or triclinic symmetry;³⁶ in the monoclinic arrangements the lateral packing is the same as in the orthorhombic form, the difference being only one of end-packing, but in the triclinic form, although the structure has not been solved in detail, it is known that there is only one molecule in the unit cell,³⁷ so that the zigzag planes of all molecules must be parallel to each other; there is no doubt therefore that this is a different type of lateral packing, not very different energetically from the more usual one. The X-ray data³¹ suggest that the alternative crystal form of the high polymers corresponds with this triclinic form of the shorter-chain hydrocarbons.

Structure of amorphous regions

It is not possible to say very much about the detailed structure of the amorphous regions; indeed, in the nature of things it is likely to vary considerably from one place to another. The angular distribution of X-ray scattering shows two maxima similar to those given by liquid short-chain paraffins and by liquid polythene itself, suggesting a similar structure; if the positions of these maxima are interpreted by the Bragg equation as if they were due to spacings between planes of atoms (a procedure for which there is a certain amount of justification) it can be said that the intense peak corresponds to a spacing of 4.5 \AA , which is rather greater than the lateral spacings of the planes of molecules in the crystals (4.1 and 3.7 \AA); it may therefore be attributed to chain molecules lying side-by-side without precise arrangement, and is obviously associated with the fact that a CH_2 chain is a roughly cylindrical object with a section diameter of about 4 \AA . The spacing would naturally be larger than in a regular arrangement. It should not be assumed from this evidence that the chains are roughly parallel: molecules lying "in contact" would be expected to be much the same distance apart at their nearest points, whatever their mutual orientation. The conception of the origin of amorphous regions given previously would lead one to

suppose that chains may often be crossed, not parallel. Possibly information on this could be obtained by analysis of the amorphous scattering distribution at low angles corresponding to spacings of 4-5 Å but this has apparently not been attempted. The presence of branch points, short side-groups, and chain ends, which are expected to be in the amorphous regions, would be expected to affect the spacing of the 4.5 Å peak only slightly. There is a weaker maximum corresponding to a spacing of about 2.2 Å; this is a second-order diffraction arising from the same structural features as those responsible for the 4.5 Å band, but it does not give any further information on the structure of amorphous regions.

Proportions of crystalline and amorphous material

Some of the properties of polythene specimens (density and modulus of elasticity, for instance) are considerably affected by the proportion of crystalline and amorphous material (see Chapter 9), and it is therefore of interest to estimate the ratio and to see how it depends on molecular structure and the physical history of the specimen. Several methods have been used, the principal ones being based on density, X-ray diffraction, and infra-red absorption measurements; all are open to theoretical criticism as far as absolute figures are concerned, but since the various methods give results which are in approximate agreement, the absolute figures are probably not seriously in error.

If the densities of amorphous and crystalline regions are d_a and d_c , the measured density of a specimen is d , the proportion by weight of crystalline material is given by

$$d_c (d - d_a) / d (d_c - d_a).$$

The density of crystalline regions d_c is known from the unit cell size to be 1.000 at room temperature, but the density of the amorphous regions is known only approximately. It has not been found possible to make an entirely amorphous polythene by rapid cooling; the best that can be done is to estimate the density of amorphous regions from the liquid density-temperature curve. Hunter and Oakes³⁸ extrapolated from the melting point down to room temperature; Ueberreiter and Orthman³⁹ starting from the liquid density at the melting point, assumed that the coefficient of expansion of the amorphous regions is the same as that of the crystals. Probably the best value to use in calculations of crystalline and amorphous content is 0.84.⁹⁶ In addition to the uncertainty involved in extrapolation over a considerable temperature interval, it is not really justifiable to assume that the density of amorphous regions in a partly crystalline specimen is the same as in an entirely amorphous specimen, for the molecules in amorphous regions might be much more strained than in an entirely amorphous specimen, owing to their attachment to surrounding crystalline regions. This is especially true in highly crystalline specimens; the structure and the density of amorphous regions may vary from one specimen to another.

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The X-ray diffraction method rests on measurements of the intensities of diffuse scattering due to non-crystalline material and sharp scattering due to crystalline regions. The plot of X-ray intensity against scattering angle (see Fig. 7.6), whether obtained directly by a photon counter method or indirectly by photography followed by microphotometry, must be resolved into crystalline and amorphous contributions, after background corrections have been made. The strong crystal diffractions from 110 and 200 planes (4.1 and 3.7 Å) are used as a measure of the amount of crystalline material; for the amorphous part, Matthews, Peiser and Richards⁴⁰ and Bryant, Tordella, and Pierce⁴¹ used the area under the main 4.5 Å peak, Hermans and Weidinger⁴² the intensity at particular angles, and Krimm and Tobolsky^{43, 44} the whole amorphous scattering over a large angular range, after correcting for incoherent and air scattering. The absolute proportions of the two phases can be calculated by referring amorphous scattering by a known amount of specimen to that of a known amount of liquid polythene⁴³, or by using

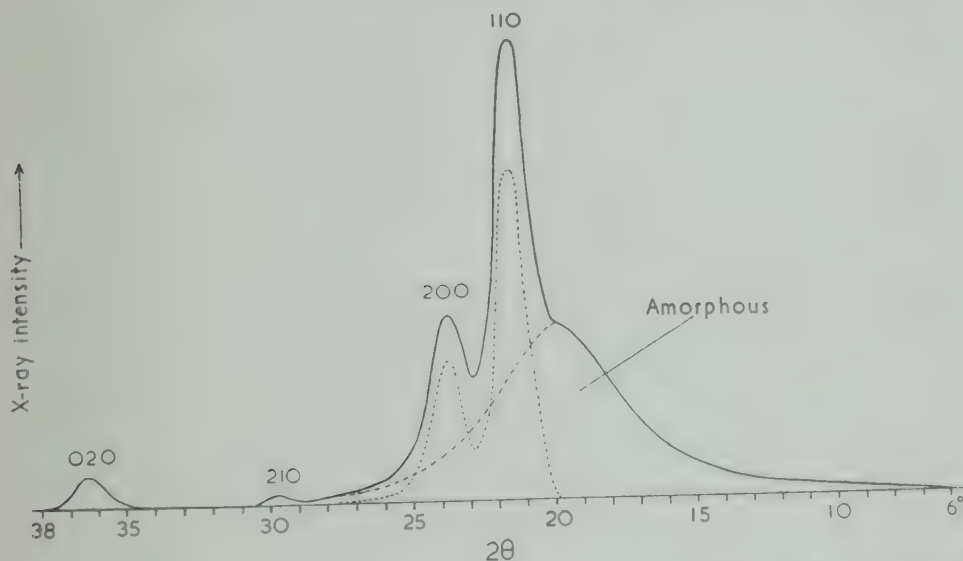


Fig. 7.6. Intensity of X-ray diffraction, in relation to angle of diffraction (after subtraction of background intensity). The curve is resolved graphically into a broad amorphous peak and sharp crystal peaks

the ratio of crystal to amorphous scattering in the principal bands after corrections have been made for various effects associated with change of scattering angle.⁴⁰ The first procedure rests on the assumption that the diffraction intensity of amorphous material at room temperature is the same as that of the same amount of liquid polythene at a much higher temperature—an assumption which is likely to be approximately correct, but more accurately so if a wide angular range is used. The second procedure assumes that the total intensity of amorphous scattering is the same as for an equal weight of crystalline material; this again is likely to be more accurately true if a wide angular range is included,⁴⁷ but since the greater part of the intensity is in the very strong peaks around

4 Å, it is probably justifiable to confine attention to these. Ideally, crystal-monochromatized X-radiation should be used, but useful results have been obtained without this refinement. Precautions should be taken to ensure that there is no preferred orientation of the crystals in the specimens or to correct for it⁴⁰ if it occurs (as it is likely to do in moulded specimens).

Infra-red methods have been based on measurements of the intensities of an absorption band at $1,305\text{ cm}^{-1}$ ($7.7\text{ }\mu$) which is given only by liquid and amorphous paraffins (the vibration assignment is unknown), and a band at 730 cm^{-1} ($13.65\text{ }\mu$) (a CH_2 deformation band) given only by crystals. For absolute proportions, the intensities of these bands must be referred to those of 100% amorphous or 100% crystalline specimens, and if measurements are made at different temperatures, it must be remembered that band intensities change with temperature. Willis and Miller,⁴⁵ for the amorphous $1,305\text{ cm}^{-1}$ band, constructed a standard curve, the high-temperature part of which is provided by liquid polythene and by C_{18-20} hydrocarbons, and the room temperature region by C_{18-20} hydrocarbons and by amorphous irradiated (cross-linked) polythene. If the crystal band at 730 cm^{-1} is used, it is important to check by X-ray diffraction that there is no preferred crystal orientation in the specimen, for this would very much affect the intensity of this band. In infra-red work it is customary to use the peak height above the background level, not the area of a peak; it is subject to the usual uncertainty about drawing in the background level, which is common to both X-ray and infra-red methods. In spite of these uncertainties, it has been found⁴⁶ that figures for amorphous content in any one specimen, obtained by X-ray and infra-red methods, usually agree within a few per cent for the normal run of polythenes and for highly crystalline polymethylenes.

Heat content measurements have been used by Raine, Richards, and Ryder⁴⁸ and by Dole, Hettinger, Larson, and Wethington.⁴⁹ In principle, the ratio of the measured heat of fusion of a partly crystallized specimen to the heat of fusion of entirely crystalline material can be assumed equal to the proportion of crystalline material in the specimen. The heat of fusion of 100% crystalline material cannot be measured experimentally, but can be estimated from the known heats of fusion of shorter-chain paraffins. In practice, the situation is complicated by the fact that the melting of polymers is not sharp; changes of crystallinity occur over a wide temperature range. It is therefore necessary to measure the heat content of a specimen over a wide temperature range up to and beyond the final melting point; if it is assumed that the extrapolated liquid curve represents the heat content of wholly amorphous material (H_a), then the proportion of crystals at any given temperature is given by

$$(H_a - H)/\Delta H_{\text{cr}}$$

where H is the heat content of the specimen and ΔH_{cr} the heat of fusion of wholly crystalline material.

MOLECULAR STRUCTURE

The results obtained by the different methods have been compared by Nichols⁹⁸ by plotting density against amorphous content given by the other methods. The amorphous content for most polythenes at room temperature lies between 20 and 50 %, and densities range from 0.96 to 0.90. For different specimens of the same density, the points obtained by different investigators by different methods lie mostly within a spread of 10 %, but the results of Matthews, Peiser, and Richards⁴⁰ are somewhat apart from the rest in the direction of lower amorphous content. The

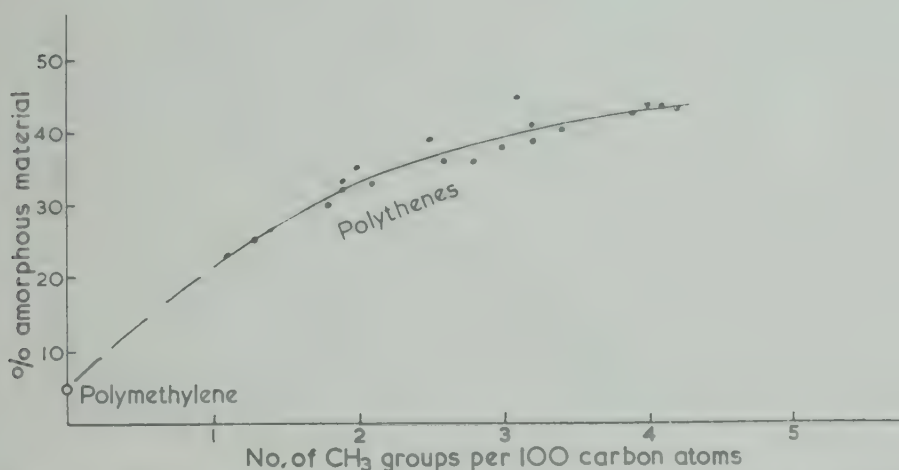


Fig. 7.7. Relation between proportion of amorphous material and degree of branching

differences are partly due to the uncertainties of extrapolation or background corrections, but may also reflect some differences of molecular structure of specimens.

There is no doubt that the proportion of amorphous material at room temperature depends chiefly on the degree of branching of the molecules as indicated by the CH_3/CH_2 ratio.^{51, 24} In general, the more branched the molecules, the higher is the proportion of amorphous material and the lower the density.^{24, 52} Fig. 7.7 shows the relation between amorphous content and branching; such a relation is to be expected, for branch points could not fit into the crystal structure. Polythene with a density of about 0.92 commonly contain 50–60 % crystalline material. Recent varieties of polythene with densities in the range 0.94 to 0.96 are much less branched and may contain 65–85 % crystalline material.⁷⁴

The proportions of crystalline and amorphous material in low density polythene cannot be altered much by thermal or mechanical treatment.³⁹ Shock-cooling of a melt increases the amorphous content by only 2 or 3 %; polythene, unlike some other crystallizing polymers, has not been obtained in entirely amorphous form even by the most drastic shock-cooling. The less branched polymers, however—low density polythene, and polymethylene, which is probably entirely straight-chained—can be as much as 90 % crystalline when slowly cooled, but only 60 % crystalline if shock-cooled. The proportion of amorphous

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material is increased by high-energy radiation, an effect which is evidently due to cross-linking of the molecules; an exposure of low density polythene sufficient to cause cross linking of 5–10% of the carbon atoms gives a product which is entirely amorphous at room temperature⁵⁵. The changes of amorphous content with temperature are described in the next section on melting behaviour.

The relation between the proportion of crystalline material and the mechanical properties is discussed in Chapter 9. Here it is only necessary to remark that amorphous polythene without cross links, if it could be obtained at room temperature, would be a soft rubbery material (it is far above its glass transition temperature—see Chapter 9), and that a partly crystalline specimen consists of comparatively rigid crystalline regions woven into the soft amorphous regions; the mechanical properties depend on the proportions of the two.

MELTING BEHAVIOUR

The melting range and final melting points of different polythenes

Polythene, like other crystalline high polymers, does not melt at a sharply defined temperature; with rise of temperature, the proportion of amorphous material increases until all the crystalline regions are melted.

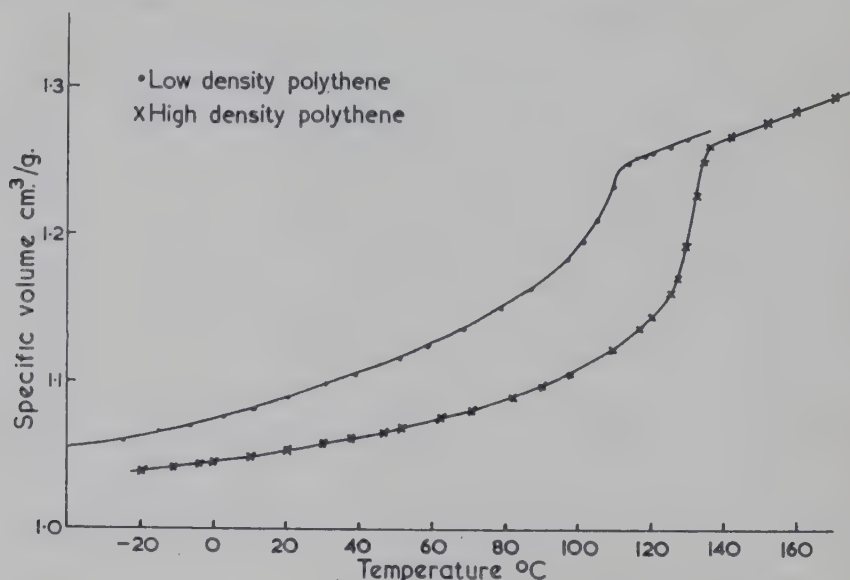


Fig. 7.8. Change of specific volume with temperature. Low density polymer, melt flow index 7; high density polymer, melt flow index not known

This is shown by measurements of the proportion of crystalline material by X-ray⁵³, infra-red and specific heat⁴⁹ methods, and by the change of specific volume^{38, 39} (see Fig. 7.8 based on measurements by Sandiford¹⁰³); in low density polythenes, the greater part of the change occurs over a range of about 15° below the final melting point, but smaller changes occur over a wide range of temperature; Trillat's X-ray results (Fig. 7.9) show that there is in fact a gradual diminution in the propor-

tion of crystalline material from room temperature upwards, but the curve becomes much steeper as it approaches the final melting point. In high density polythenes, melting occurs more sharply and at a higher temperature.

This gradual melting is due primarily to the two-phase texture resulting from the crystallization of a tangle of very long molecules; qualitatively, one may imagine that, since the movements of molecular segments are more free in the amorphous than in the crystalline regions, rise of temperature would be expected to make some strained molecular segments on the crystal boundaries leave crystalline regions and become part of the amorphous fraction; and small crystals will melt completely before

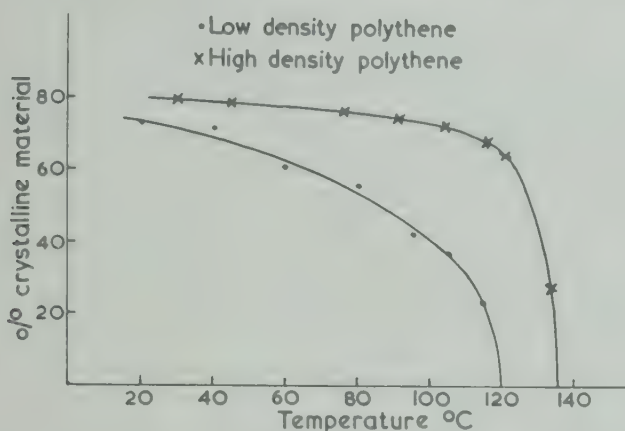


Fig. 7.9. Change in proportion of crystalline material with temperature. Low density polythene measured by X-ray method (Trillat et al.⁵³); high density polythene measured by infra-red method (Miller¹⁰⁴)

the larger ones are dispersed. There is probably a continuous reorganization in the sense that some crystals melt while others grow (depending on local constraints), but the net result is that the proportion of amorphous material grows with temperature. Alfrey and Mark⁵⁴ suggest that during crystallization, owing to the constraints imposed by crystals on neighbouring amorphous segments, each successive amorphous chain unit is more difficult to fit into the crystal; the change of entropy ΔS on crystallizing is therefore greater for the later units. If it is assumed that the heat of crystallization, ΔH is the same for each unit, then the blurring of the melting point $T_m (= \Delta H / \Delta S)$ may be regarded as due to this variation of ΔS . Frith and Tuckett⁶⁴ showed that the free energy of a system of crystallites and amorphous regions is a non-linear function of the proportion of the amorphous material, and that there is a certain proportion of amorphous material corresponding to a minimum free energy, and hence to the thermodynamic equilibrium at any temperature below the final melting point; their expression for the change of amorphous content with temperature is in general agreement with experimental results.

These treatments apply to high polymers in general, and say nothing about the effect of a spread of molecular weights in the specimen, or of

chain branching; they are most relevant to polymethylenes and high density polythenes, which melt more sharply and at higher temperatures than lower density polythenes; polymethylene melts finally at 136.5°C ,⁶⁸ lower density polythenes at $110\text{--}115^{\circ}\text{C}$, while high density polythenes are intermediate, melting at $125\text{--}131^{\circ}\text{C}$.⁷⁴ The spread of molecular weights in a specimen is not expected to influence the final melting point or the melting range unless there is an appreciable proportion of small molecules of molecular weight below 1500 (i.e. less than 100 carbon atoms, smaller than the average crystal diameter). Richards⁶⁵ has extended Frith and Tuckett's treatment to cover specimens containing such low molecular weight material, of which there is an appreciable proportion in low density polythenes. Part of the difference between their melting behaviour and that of polymethylenes is due to this cause, but in addition the branched structure of the molecules is expected to have an effect on the melting behaviour similar to that of low molecular weight material: the final melting point and the melting range are bound up with the proportion of amorphous material at room temperature, which is inevitably increased by chain branching. Flory's theory⁶⁷ of the melting points of copolymers is relevant here; when chain units which do not fit into the crystal structure are present, the melting point is depressed to an extent depending on the proportion of non-fitting units and the latent heat of fusion of the crystals.

The term "melting point", if used without qualification, refers to the temperature at which the last crystals melt. This point is most satisfactorily defined by dilatometer measurements over a range of temperature around the melting point; the steep change of density or specific volume which accompanies final melting (Fig. 7.8) defines the final melting point to within 1°C , but to obtain reproducible results it is necessary to take the material through very slow cycles, especially for unbranched polymers of very high molecular weight. The work of Mandelkern and his collaborators^{66, 68} shows that observed melting points are increased several degrees by such treatment, and indicate that most recorded figures for high polymer melting points are not true equilibrium values. The determination of the equilibrium value by this method is such a lengthy task that in the normal evaluation of polymer samples it is not likely to be often attempted. Approximate values of the final melting point, lower than the equilibrium value but comparable from one sample to another, can be obtained by observing the temperature at which a heated sample becomes transparent or liquid; but the best method of general purposes is to observe, under a polarizing microscope fitted with a heating stage, the point at which a thin film of the material, on a microscope slide between crossed polarizers, ceases to show the interference illumination due to the birefringence of crystal aggregates; in this method final melting points near the equilibrium values are obtained with heating and cooling rates of 1°C per minute.⁷⁶

It is often observed, in such experiments, that on repeated melting and recrystallization, some spherulites reappear in the same places;

this occurs not only in polythene but in other polymers also. Whether this is due to nucleation on extraneous solid particles or particular places on the surface of the microscope slide, or whether it means that certain molecular aggregations suitable for the formation of crystal nuclei persist above the melting point, is a matter for conjecture, but whatever the cause, the phenomenon must influence the kinetics of crystallization. In some other polymers, the course of crystallization is markedly dependent on the thermal history of the melt;^{57, 75, 77} these nucleation centres are only destroyed at temperatures many degrees above the melting point.

Polythene in comparison with other polymers

The melting point of polythene may be said to be in the middle of the spectrum of melting points presented by the various crystalline polymers which are in general use: it is much higher than those of the rubber-like polymers and aliphatic polyesters, and much lower than those of the nylons, aromatic polyesters and polytetrafluoroethylene. Three molecular characteristics appear to play a dominant role in determining the melting point of a high polymer:⁷⁸ the cohesive forces between the molecules (best expressed as molar cohesion energy per rigid chain unit), the flexibility of the chains, and the general shape of the molecule. The cohesive forces in polythene are comparatively weak, owing to its hydrocarbon character (the only polymers with much weaker cohesive forces are the silicones); weak cohesion would favour a low melting point, but in other respects the CH_2 chain has characteristics which increase the melting point. It must be regarded as a moderately flexible, moderately stiff molecule, much more rigid than the molecules of rubber or the aliphatic polyesters, though not so rigid as the CF_2 chain. Finally, the symmetrical, fairly streamlined shape of the chain would tend to increase the melting point; this effect of shape is not due to efficient packing in the crystal, for the chains are no more efficiently packed than those of the aliphatic polyesters; it is probably due to an influence of shape on the pattern of molecular vibrations in the crystal. Symmetrical streamlined molecules, in the course of their vibrations in the crystal, disturb their neighbours less than the more awkwardly shaped molecules: there is less interlocking of molecules, and less interlocking of the different modes of vibration throughout the crystal.

SPHERULITE STRUCTURE

Thick specimens of polythene, like those of other crystalline polymers, are opaque. The scattering of light responsible for the opacity is not due to individual crystalline regions, which are much smaller than the wavelength of visible light; it is due to larger structural units. Microscopic examination of thin films or sections between crossed polarizers reveals a general illumination interrupted by extinction crosses which are evidence of the presence of units of radial structure (see Plate 7.2).

The extinction cross is familiar to crystallographers and mineralogists and in inorganic and monomeric substances is produced by an assemblage of crystals radiating from a point; it is usually due to the growth of a large number of crystals outwards from a point, all with the same crystallographic axis pointing outwards. The arms of the black cross, which are parallel to the vibration directions of the polarizers, are due to crystals in their extinction positions; crystals in intermediate orientations are illuminated. Most crystalline polymers have this type of structure, and observation of slowly cooling thin films confirms that the spherulites are formed by outward growth from nucleation points: growth continues until neighbouring spherulites meet. In some preparations the boundaries between spherulites are well-marked straight lines, but more often the appearance is rather diffuse; this is partly because different spherulites overlap in the line of vision.

Illumination between crossed polarizers occurs because the material is birefringent—that is, the refractive index varies with the vibration direction of the electromagnetic waves, and this in turn is evidence of molecular orientation. It has been shown³³ that in polythene spherulites the refractive index is greater for the tangential than for the radial direction, and this negative birefringence is clear evidence that the chain molecules are tangentially disposed: the crystals must be oriented so that the *c* axis (the molecular chain axis) tends to be tangential. X-ray micro-beam diffraction photographs of portions of spherulites taken by Keller⁵⁰ confirm this, and provide the further information that it is the *b* axis of the crystals that tends to lie along the spherulite radius.

Bryant⁵¹ found that the birefringence—the difference between tangential and radial refractive indices—is very small (0.002 to 0.003), not more than one-tenth what it would be if tangential orientation of the molecules were perfect; there must be considerable dispersion of molecular orientation. The appearance of electron microscope photographs of very thin films at very high magnifications (see Plate 7.2) is consistent with this conclusion: each spherulitic unit shows radiating fibrils, but there is much meandering and branching; if we can assume that the fibril directions represent crystal growth directions, it is evident that the radial orientation of the *b* axes of the crystals is far from perfect. It should be remembered that birefringence is a measure, not of crystal orientation, but of the total molecular orientation of crystals and amorphous material together; nevertheless, since spherulite formation is a crystal growth phenomenon, the orientation of the crystals is the primary consideration. Keller's X-ray micro-beam diffraction photographs⁵⁰ again confirm that there is much dispersion of orientation of the crystalline regions. It is also possible that the very weak birefringence of the spherulites is due to reversed orientation in crystalline and amorphous regions: molecular segments which are tangentially oriented become incorporated in the crystals, leaving the radially oriented segments to constitute the amorphous regions. In the viscous liquid there is not time for the extensive reorganization which would be necessary for a high

degree of uniform orientation, so the structure as a whole is not very different from that of the original random tangle of molecules.

The centres of spherulites are often sheaf-like in appearance; this suggests that each spherulite originates in a single crystal nucleus, which grows at first into a rod-like form, but soon splays out at the ends, with more and more distortion and branching until a complete radial structure is set up. The crystallographic direction which becomes dominant along the radii of the spherulite would be, by natural selection, the most rapidly growing direction; it appears therefore that the b axis of the crystals, one of the directions at right angles to the chain axis, is the direction of most rapid crystal growth. The simplest molecular picture of crystal growth to which these considerations lead is the following. Crystal nucleus formation presumably occurs at those rare places where sections of a number of chains happen to be lying roughly parallel to each other; growth may then occur either longitudinally by progressive straightening along the same molecules or laterally by accretion of sections of other molecules. The established facts already mentioned indicate that growth along one of the lateral crystal directions, the b axis, occurs most readily. It is not obvious why it is the b axis rather than the a axis or any other direction in the $a b$ plane, but it does seem reasonable that lateral growth should be easier than growth along the chain axis. Growth in any direction occurs under difficulties, owing to the vast tangle of molecules in a liquid polymer, and this is why distortion and branching occur, but growth by progressive molecular straightening along the chain axis would appear to be extremely difficult, because the many molecules in the crystal presumably wander off into the tangle in all directions, and disentangling could occur only very slowly, even if the molecules were unbranched; in low density polythene the branching also plays a part in limiting crystal growth along the chain axis. On the other hand, crystal growth in lateral directions needs only the straightening and re-orientation of the nearest pieces of *any* neighbouring chains, a process which can continue indefinitely and without a major disentangling operation. This appears to be the simplest explanation of the tangential orientation of chains in spherulites, which has been shown⁵⁰ to occur in other crystalline polymers as well as polythene. The sort of structure envisaged is sketched in Fig. 7.4.

A very different and much more elaborate picture has been put forward by Keller⁵⁰ and Morgan,⁵⁷ who suggest that long fibrillar crystals, elongated along the *chain* axis (c), are coiled into helices, and that a spherulite consists of an assemblage of such helices radiating from a point; to account for the tangential orientation of the chains shown by the negative birefringence, the helices would have to be closely coiled so that the angle between the chain and the helix axis is more than 54° . To the writer, extended growth along the chain axis seems unlikely for the reasons already given, especially in low density polythene with its branched molecular structure; and there is no good electron-microscopic evidence for the existence of closely-coiled helices,⁵⁸ for the radiating

fibrils (down to 100 Å thick) do not curl helically but meander and branch out irregularly, and within the fibrils there is no room for curling, for the molecules in crystalline regions are known (from X-ray diffraction evidence) to be straight for 100 Å or more. (Apparent rope-like twists on the scale of a few hundred Å have been seen in thin films of polyamides⁷³ and polyesters,⁵⁸ but they occur only here and there, and do not appear to be general features of the structure; they seem to occur no more frequently than would be expected by chance in an essentially random meandering of the fibrils).

Some polythene specimens, crystallized just below the melting point, show, instead of the normal extinction cross, a concentric ring extinction pattern⁵⁶ which Keller interprets as an extreme form of the zig-zag extinction cross seen in some other polymers, and which does suggest a helical structure on the large scale of 10,000–100,000 Å. Electron micrographs do not show⁵⁸ any obvious signs of such a structure, but it must be remembered that the optical birefringence is so small that it means only a slight departure from randomness—perhaps a regular veering of the mean growth direction which would not be obvious in the meandering and branching fibrillar structure. Such a structure might arise from some stress-orientation effect in the crystallizing liquid, due to contraction on crystallization.^{59, 60} In short, present evidence does not support the suggestion of a helical structure on the small scale of 100 Å or the picture of fibrillar growths along the molecular chain direction, coiled into flat helices; but optical evidence does suggest some sort of helical structure on the large scale of 10,000–100,000 Å (1–10 μ), similar to that found in some spherulites of monomeric and inorganic substances.⁵⁶ The occurrence of this type of structure in non-polymer spherulites suggests that it does not depend on chain molecules; it may be connected with circumstances which seem to be common to spherulite formation in both polymer and non-polymer substances—crystallization from a viscous liquid or gel: circumstances which are likely to give rise to stress-orientation in the crystallizing liquid or gel. The mechanism by which stress-orientation in the liquid may result in a statistically helical crystal growth is not clear, but, as Schuur^{59, 60} has pointed out, polymer crystallization is accompanied by contraction normal to the chains, and this gives rise to a reversed orientation in the neighbouring liquid; in exceptional cases this may result in a reversed orientation in neighbouring crystals, but in general we may expect not alternation but continuity, and a helical succession of orientations is one which is compatible with growth statistically in one direction (the spherulite radius) and with continual change of orientation. The change of orientation could be random, and electron micrographs of polymer spherulites suggest that for the most part it is, but some tendency for a uniform change of direction is perhaps to be expected in a process influenced by liquid flow and stress orientation in the liquid.

The thickness of the radiating fibrils seen in electron micrographs of polythene spherulites—down to 100 Å—agrees with the figure for crystal

size given by the breadths of X-ray diffraction lines; but it is necessary to point out that the diffraction lines from different crystal planes are usually of similar breadth, suggesting at first that the crystalline regions have much the same dimensions in all directions, whereas the evidence on spherulite structure which has already been discussed suggests that the crystals are a few hundred Angstrom units in size in the chain direction but very much larger than this in lateral directions—indeed, it may be that there is continuity of crystal structure along a fibril from the centre to the boundary of a spherulite. There is, however, no real inconsistency: X-ray diffraction lines may be broadened by disorder or distortion in the crystals as well as by small size, and it is presumably the meandering and branching which is responsible for the broadening of those X-ray diffraction lines associated with crystal planes parallel to the chain direction. In other words, it is accidental that diffraction broadening is much the same for all crystal directions; it is perhaps justifiable to say that in the long distorted fibrillar crystals, the small regions which can be considered perfect are of similar dimensions in all directions.

The scattering of light responsible for the opacity of polythene specimens occurs in several different ways. Some of the light is undoubtedly scattered at the boundaries between neighbouring spherulites, but it must not be supposed that there are definite cracks; on the contrary, the crystalline regions in neighbouring spherulites are probably knit together by molecules threading through both. Nevertheless, there may be a higher proportion of amorphous material at the boundaries, and therefore a change of refractive index; moreover, a sudden change of orientation of the birefringent crystalline regions in passing the boundary between one spherulite and the next is itself associated with an abrupt change of refractive index which is a cause of light scattering. In addition, radial rib-like markings on the optical scale are often seen inside large spherulites; they represent the coarser features of the radial structure revealed by the electron microscope, but poorly resolved by visible light; some scattering of light occurs here also. The degree of opacity of a specimen would depend on the average size of the spherulites, the abruptness of the boundaries in terms of refractive index differences, and on the coarser features of the internal structure, but no attempts at experimental study of the influence of these factors have so far been made. Hawkins and Richards⁷² measured the light transmission during heating and cooling; with rise of temperature there was a continuous increase of light transmission up to the melting point, which is no doubt associated with the increase in proportion of amorphous material, accompanied probably by a "softening" of the optical discontinuities; but on cooling from the melting point, the light transmission first decreased, then increased, and finally decreased again—changes which are presumably associated with the growth of spherulites, their meeting at definite boundaries, and subsequent changes of refractive index on cooling; precise explanation is scarcely possible. High density polythene tends to be more opaque than

the low density specimens;⁷⁴ two factors which contribute to this difference are the higher crystallinity of the high density polymer (there is less amorphous material to "soften" the spherulite boundaries), and the tendency to form larger spherulites.

It would be expected that the mechanical properties of polythene specimens would be influenced in some degree by spherulite size, though the influence of size in itself may well be less than that of crystal size in monomeric and metallic substances, for spherulite boundaries are not the abrupt discontinuities found in non-polymers. Experimentally, it is not easy to disentangle the influence of spherulite size from that of other differences in texture; for instance, it is known that rapid cooling, which decreases spherulite size, tends to give specimens which are more flexible than slowly cooled or annealed specimens, and the reduction in modulus is greater than would be expected from the small decrease in the proportion of crystalline material.¹⁰⁶ It is not certain, however, that this effect is due to spherulite size in itself; annealing or slow cooling leads to molecular re-organization in various ways—the size and perfection of the crystalline regions would be affected, as well as the local strains in the amorphous regions; the difference of spherulite size is only one of several effects, and not necessarily the most important, though it is the most obvious.

The impression of a very definite "grain size" which the spherulite structure gives is in some ways misleading. It should be remembered that the degree of local orientation in a polythene spherulite is quite small: there is really only a slight departure from randomness of orientation, due to the fact that crystallization occurs in a viscous liquid consisting of a vast tangle of long-chain molecules. The outward growth of crystals from nucleation points gives rise to a certain amount of radial orientation, but extensive disentangling of molecules is impossible in the time usually taken in crystallization, so that the ultimate structure is not very different from that of the initial tangle, except for the very local straightening of groups of molecular segments a few hundred atoms long to form the crystalline regions. The crystalline and amorphous regions are woven together by molecules passing through both (and not only within spherulites but also across spherulite boundaries) and it is this crystalline-amorphous texture that is the basis for the characteristic mechanical properties of crystalline polymers, which can be attributed to the reinforcing effect of rigid crystalline regions woven into the softer amorphous matrix. The effects most likely to influence mechanical properties—imperfections and dislocations in the crystalline regions, and local strains in amorphous regions—are unfortunately those most difficult to study experimentally.

Spherulite size is decreased by very rapid cooling,⁷⁴ showing that there is a rise in the rate of nucleus formation with falling temperature. Some polymers (and indeed some monomeric substances) can be obtained in amorphous form by sufficiently rapid cooling, showing that the rate of nucleus formation declines again at low temperatures,^{57, 75} but polythene has not been obtained in entirely amorphous form even by shock cooling

in liquid air. The very ready crystallization of this polymer may be ascribed to its simple symmetrical molecular structure and short chain repeat distance: if, in the liquid, neighbouring chains are not in suitable positions for forming the crystalline arrangement, they do not have to move far to attain these positions. In the subsequent growth of crystal nuclei, the spherulite radius increases at a constant rate at any given temperature (as in other polymers): this would be expected from the fibrillar structure. The net rate of crystallization of a specimen at a given temperature is a function of both nucleation and growth rates. Reding and Brown,¹⁰⁷ in a study of the rate of crystallization by measurement of the change of intensity of the 730 cm^{-1} infra-red absorption band which is due to crystals only, found that the net rate for any one specimen increases rapidly as temperature falls; this is probably due to the rapid rise of nucleation rate as the temperature falls. Differences in the rates of crystallization of different specimens seem to be correlated with the degree of branching of the molecules: as might be expected, the more highly branched molecules crystallize more slowly.

STRUCTURE OF STRESSED OR WORKED SPECIMENS

When a polythene specimen is stressed, it exhibits a general birefringence superimposed on the local effects due to the spherulite structure; tension produces positive birefringence (the refractive index being higher along the direction of stress than at right angles to it), compression the reverse. This could be due either to stressing of interatomic bonds (as in hard glasslike bodies) or to the molecular orientation which accompanies the deformation of the specimen; Crawford and Kolsky⁷⁹ found that in stretching, the relation between strain and birefringence is linear up to strains of 0.25, and this is consistent with the change of orientation of rod-like crystals in an elastic matrix. The relation of stress to birefringence, however, is not linear, and there are large hysteresis effects; the structure does not return to its original state when the stress is removed. It is likely that orientation of molecules in both crystalline and amorphous regions is the principal origin of the birefringence: we may imagine the segments of molecules in the amorphous regions tending to become parallel to the direction of stretching, and the more rigid crystalline regions being pulled by the tie molecules so that the molecular chain axes in these also turn towards the direction of stretching. This change of orientation would produce positive birefringence. (Note that if the growth fibrils of the spherulites (the b axes of the crystals) were to turn towards the direction of stretching, this would produce negative birefringence; so this is evidently not the mechanism).

Cold-drawing and the structure of fibres

Larger strains at room temperature produce, in fibres and films, the phenomenon of 'cold-drawing'; the specimen does not become thinner gradually; it becomes thinner suddenly at one point, shoulders are

developed where the drawn thin fibre joins the undrawn thicker part, and subsequently the shoulders travel along as more material passes from the undrawn to join the drawn portion, the thickness of which remains constant at one-half or rather less than half that of the original specimen; the lengthening is to some four to six times the original length. (See Chapter 9.) No further elongation can be achieved: any attempt to do so merely results in breaking the specimen. The extension is irreversible at room temperature: the specimen remains extended when released. Cold-drawing, although it was first noticed in crystalline polymers, and is exhibited most readily by them, is not peculiar to them; it has been produced in an amorphous polymer,⁸⁰ and on the other hand it can be avoided in crystalline polymers by sufficiently slow drawing. It arises from the adiabatic nature of the extension and a particular relation between modulus and temperature; the phenomenon has been discussed from this point of view by Marshall and Thompson.⁸⁰ From the molecular point of view, the outstanding change which occurs is that the crystalline regions become oriented so that their c axes (the chain directions) are parallel, or nearly so, to the fibre axis; this is shown by X-ray diffraction photographs of drawn fibres, which show crystal reflexions as short arcs instead of the complete rings given by unoriented specimens (see Plate 7.1).

The arcs on the equator of the photograph are from crystal planes parallel to the chain axis; the others are from inclined planes. The diffuse scattering at 4–5 Å due to amorphous material, on the other hand, is still a complete ring; the intensity is not uniform, and is somewhat larger on the equator than on the meridian, but it is evident that orientation in the amorphous regions is very poor compared to that developed in the crystalline regions. The structure is evidently as shown in Fig. 7.10.

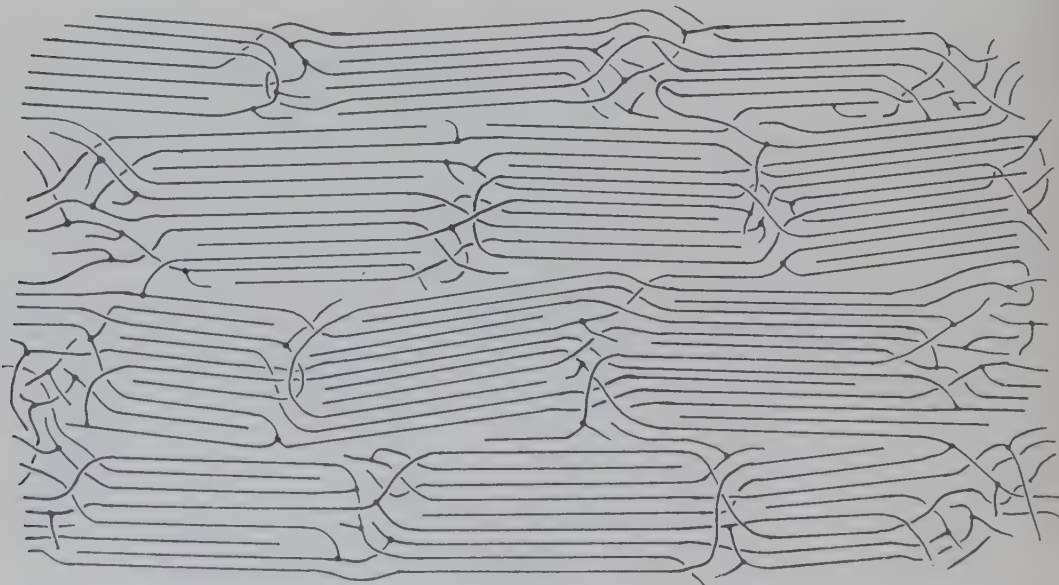


Fig. 7.10. Molecular arrangement in a drawn fibre. Orientation is much better in crystalline than in amorphous regions

MOLECULAR STRUCTURE

The phenomenon of cold-drawing presents two interesting problems—the molecular mechanism by which the reorganization takes place, and the remarkably definite reduction of thickness and increase of length, which is similar not only in different polythene specimens but in other crystalline polymers. On the molecular mechanism, it can be said that the change of structure involves the pulling of the molecules out of the original tangle into parallel position; it is a molecular “drafting”, to use the textile term, and this must mean that crystals are pulled to pieces in the process. Subdivision may go as far as individual molecules, for it has been found that when the triclinic form is present in the original sample, it is converted into the orthorhombic form on drawing;³¹ this change necessitates either the disruption and re-formation of crystals, or molecular rearrangement within the crystals. The subdivision occurs at the shoulder region, where the heat developed in the process (the work done in drawing) accumulates; the rise of temperature here increases the proportion of amorphous material and increases molecular mobility. The process can be regarded as partial melting: the material goes through an amorphous stage, not necessarily *en masse* but locally and progressively. There is practically no net change in density or in the proportions of crystalline and amorphous material as a result of the drawing process, but Krimm and Tobolsky⁴³ found, by measuring the breadths of X-ray reflexions, that there is apparently a considerable reduction of size of the crystals: the apparent lateral crystal dimension in their specimen decreased from 140 to 59 Å. (This was a low density specimen with only 40% crystalline material present at the start—evidently a highly branched polythene; the change of apparent crystal size on drawing would depend on the structure of the initial specimen, and on the conditions of drawing. It should also be remembered that X-ray reflexions are broadened by distortion as well as by small size; what is being measured is the effective size of the small perfect regions).

The remarkably definite draw ratio and reduction of thickness has not been explained quantitatively. It is true that the draw ratio does depend to some extent on the conditions of drawing, and if the temperature is increased sufficiently the shoulder effect becomes less definite until ultimately the cold-drawing process is replaced by a gradual thinning without a definite draw ratio; nevertheless the fact that at temperatures far below the melting point the draw ratio is of the same order (four to six times) for specimens of widely different molecular weight and different degrees of branching, and even for chemically different polymers, including polyethylene terephthalate which starts amorphous and only crystallizes on drawing, is a very striking one which calls for a molecular explanation. Qualitatively it can be said that when the molecules become for the most part parallel to the fibre axis in the drawn portion, it is much harder to drag them past each other than it is to start the drawing process in the original randomly oriented specimen, just as it is much harder to pull adhesive tape along the adhering surface than it is to strip it off progressively by pulling at an angle to the adhering surface;³³ but it is

still not known why the draw ratio should be four to six times (with an accompanying reduction of diameter to one-half or a little less) for a wide range of conditions and specimens. It would appear to be a fundamental characteristic of the chain molecule structure of these plastic materials.

The change of orientation of the crystals in cold-drawing, from random to parallel positions, does not occur in a quite straightforward manner: in specimens drawn very slowly without necking, and in the shoulder region of more rapidly drawn necked specimens, the crystals tilt over in a special way (or perhaps they re-crystallize in a special way), such that the 100 plane becomes parallel to the fibre axis first, to be followed later by other *hkO* planes.^{81, 83} It has also been stated that there is a preferred angle of tilt of 27° ⁸² (at first given⁸¹ erroneously as 64°), but this has been disputed.⁸⁴ The preferred parallelism of the 100 plane may be due to easy slipping on this plane. An alternative explanation by Point⁸⁷ which would account for the parallelism of this plane and in addition would lead to a preferred angle of tilt not far from the reported 27° is that twinning occurs by the bending of the molecules to a *cis* configuration; but Holmes⁹⁶ finds that a *gauche* configuration at the twin plane, which is stereochemically more probable, also gives a preferred angle of tilt which is nearer to the reported 27° .

A preferred orientation also occurs when a fibre is heated to a temperature not far below the melting point (105° to 110°C) and allowed to contract freely; the crystals become disoriented in a special way, but the plane which remains most nearly parallel to the fibre axis in these circumstances is 010, not 100.^{81, 83} A similar difference between the preferred orientations in drawing and in relaxing occurs in nylon 66.⁸⁵ It has been suggested that the preferred orientations are connected with the coefficients of expansion in the different crystal directions,⁸³ but the mechanism is not clear.

The retraction which occurs on heating nearly to the melting point is not complete; specimens do not regain their original dimensions. The retraction is due to the tendency of the molecules to curl up as the result of random thermal motions of the chain units; at room temperature the orientation is frozen into the recrystallized material, but as the temperature approaches the melting point, molecules are released from the crystals and curl up. The incompleteness of the retraction means that there has been irreversible slipping of the molecules during drawing, just as in the stretching of unvulcanized rubber. Completely reversible extension can only be attained by cross-linking the molecules, as in vulcanized rubber.

The distribution of X-ray scattering at very small angles to the primary beam, for drawn polythene fibres, shows maxima at angles which indicate periodicities in the fibre of 100–200 Å.⁸⁶ This figure is similar to the apparent crystal size calculated from the breadths of large-angle diffractions, and it indicates that for fibres at any rate the broadening of the large-angle diffractions is due to small crystal size and not to distortion

of larger crystals. There is another feature of the small angle scattering pattern which is somewhat surprising: Arnett, Meibohm, and Smith⁸⁶ found that the maxima occur as discrete spots which are not on either the equator or the meridian of the photograph, but form a pattern which indicates some approach to three-dimensional regularity in the arrangement of the crystals—a sort of superlattice, a crystalline arrangement of small crystals. Relaxation leads to some increase of crystal size. A possible explanation is that the crystalline regions are of approximately uniform size; some regularity of arrangement would be expected in these circumstances, for the same reason that spheres or soap bubbles of uniform size have a strong tendency to form regular arrangements.

An interesting application of stress-birefringence measurements of cross-linked polythene has given some information on the flexibility of the chains. Polythene, when cross-linked by electron bombardment, behaves like vulcanized rubber above its melting point, and stretches reversibly. Volungis and Stein⁸⁸ measured the birefringence and the stress at temperatures from 120° to 170°C, and from Treloar's equation⁸⁹ calculated the anisotropy of polarizability of the apparent statistical chain segment. (In the treatment, a chain is regarded as a string of rigid, freely jointed segments). The figures indicate that the statistical segment is about 30 carbon atoms long—much longer than the segment in rubber, which is 1.4 isoprene units or about 6 carbon atoms long. The CH₂ chain does not, of course, consist of rigid segments 30 carbon atoms long which are freely jointed; it is semi-flexible at each chain bond, rotation round which is hindered by an energy barrier; the figures indicate that it is considerably more stiff than the rubber molecule. This conclusion is consistent with the melting points of the two substances.⁷⁸ From the small decrease in apparent segment size with rise of temperature, Volungis and Stein calculated the energy barrier hindering bond rotation, and obtained a figure, 6.4 kcal. per mole, considerably higher than that obtained for *n*-butane vapour—4 kcal.;⁹⁰ the difference may be attributed to additional hindering effects of surrounding molecules in the solid.

Pressed, rolled, and two-dimensionally stretched sheets

In pressed sheets the crystalline regions take up a preferred orientation in which the 110 plane tends to lie in the plane of the sheet. In specimens thinned by passing through rollers, this same crystal orientation is found, in addition to the orientation of the chains (the *c* axis of the crystals) parallel to the direction of rolling;³⁰ and in sheets stretched two-dimensionally, as in the experiments of Hopkins, Baker, and Howard⁹¹ in which sheets were blown into bubbles, again the same plane orientation of the crystals with 110 in the plane of the sheet (and the chains randomly oriented in the plane of the sheet) is observed. The prevalence of this plane orientation probably means that 110 is the best cleavage plane in the crystal: when crystals are pulled to pieces during the re-organization that has to take place, they part most readily along the 110 planes. It is reasonable that this should be so, for the 110 plane exhibits the greatest

density of molecules in the plane and the greatest spacing between successive molecular planes. This orientation means that the chains tend to lie in the plane of the sheet; this again is natural—it is found in crystalline polymers generally, and to a lesser degree in non-crystalline polymers.

Extruded specimens—films and wire coverings

In specimens made by extrusion of liquid polythene, where crystallization occurs during subsequent cooling, some degree of orientation is found, which can be ascribed partly to the molecular orientation set up in the liquid by the extrusion process and partly to other effects such as non-uniform nucleus formation in a flowing and partially oriented liquid, and the change of orientation which occurs during relaxation of the partly crystalline material at temperatures a little below melting point.

Polythene wrapping film is made by extruding the viscous liquid through a narrow slit and allowing it to cool; the slit may be linear, giving a flat film, or circular, giving a tubular film which can be packed flat and slit afterwards. The wind-up system is very nearly tensionless to prevent drawing of the film; nevertheless the film produced does exhibit orientation in both crystalline and amorphous regions. Holmes and his collaborators⁹² found that the X-ray diffraction patterns of flat film are consistent with a crystal orientation in which the a axis lies along the machine direction and the other axes are randomly disposed about a ; but Keller⁸⁴ found, in laboratory specimens, evidence in favour of a different scheme of orientation in which the b axis lies perpendicular to the machine direction, with a random disposition of the other axes around b . It is not possible to distinguish between these two when there is considerable dispersion from the ideal, as there usually is in commercial film, but it seems likely that both types can occur. The type described by Holmes is that which arises during relaxation below the melting point.^{81, 83} The other type could arise, as Keller has suggested,⁸⁴ by the formation of crystal nuclei in lines along the machine direction, spaced more closely along the machine direction than at right angles to it; the resulting spherulites, growing outwards until they met, would be flattened in the machine direction, and since the b axis is along the spherulite radius, the observed orientation is set up.

Molecular segments in the amorphous regions are oriented in a different way: the chain axes, according to the evidence of birefringence for visible light and the dichroism of the infra-red absorption band at 721 cm^{-1} , tend to be parallel to the machine direction, though there is much dispersion.⁹² This orientation of the amorphous regions is probably a relic of the chain orientation set up in the extruded liquid; when the liquid crystallizes, those chain segments which are suitably oriented become incorporated in crystalline regions, leaving the others to constitute the amorphous regions. Reversed orientation in crystalline and amorphous regions is likely to occur whenever crystal orientation, which is subject to its own special principles, differs from that prevailing in the liquid; it has already been mentioned that it may well occur

locally in the spherulites formed in unoriented specimens. It will be evident that, as there are several influences at work, the orientation is likely to vary considerably with the properties of the polythene and the conditions during the formation of the film: the degree of chain orientation in the liquid will depend on the molecular structure and the temperature, and any crystal orientation effects of relaxation will depend on the rate of cooling through the critical temperature range. The overall orientation (of crystals and amorphous parts together) is shown by the birefringence figure to be quite small: the birefringence is often less than 0.01, which is a small fraction of the figure for perfect chain orientation, 0.06, calculated from the polarizabilities of the bonds.⁹⁷

The orientation in the polythene coverings of submarine cables was studied by Kortsch,⁹¹ by measuring the birefringence of thin sections cut with a microtome. In transverse sections he found a very small birefringence, usually not more than 0.001; but there is a reversal of sign about halfway between the wire and the outside, the inner zone having the higher refractive index tangential while the outer zone has it radial (and there is a transition region where the birefringence is zero). In longitudinal sections the birefringence was usually higher (up to 0.0025), with the higher refractive index nearly always parallel to the direction of extrusion, except in specimens made with a very low cooling temperature of -40°C , which had a normal inner zone but an outer zone with reversed orientation. Since the longitudinal birefringence was usually higher than the transverse, it appears that the highest of the three refractive indices for the three principal directions was usually parallel to the direction of extrusion, which would be consistent with a tendency for the chain molecules to lie in this direction, as might be expected; but the interpretation of the other two refractive indices and the zonal variations in terms of the flow and stresses in the cooling material would appear to be very uncertain. The problem would be clarified if orientations in crystalline and amorphous regions separately were studied by integrating the results of optical, X-ray, and infra-red examination, as was done for polythene film. This work on cable coverings was undertaken in connection with tests for environmental cracking (see Chapter 10), which is known to be much accentuated by biaxial or triaxial stressing;⁹¹ Kortsch found that the use of a very low cooling temperature of -40°C reduced the tendency for environmental cracking; these conditions tend to give a greater transverse birefringence but a lower longitudinal birefringence, and the effect of this combination on environmental cracking is very difficult to judge. It may well be that a slight increase in the proportion of amorphous material which takes place on rapid cooling is important as well as the orientation in the material.

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CHAPTER 8

DIELECTRIC PROPERTIES

D. W. McCALL

POLYTHENE is a polymer whose insulating properties compare favourably with those of any known dielectric material. As such it received rapid acceptance in all manner of applications and the dielectric properties have been extensively investigated over the past ten years. On examination of the vast amount of data available on this substance one is led to the conclusion that polythene is a well-behaved dielectric and is probably better understood than any other commercial dielectric material. However, the description is still far from complete and much more needs to be done to characterize the material.

While the structure of polythene is related to that of the normal paraffins¹ it differs from that structure in a number of ways.² Much literature has appeared on this subject,^{3, 4, 5, 6} and since structure has a bearing on the dielectric properties reference should be made to the full treatment given in Chapter 7 of this volume.

THE DIELECTRIC CONSTANT

The discussions of the dielectric constant and loss will be made on the basis of the Clausius-Mosotti-Debye^{7, 8, 9, 10, 11} equation because it is familiar and holds fairly well for non-polar substances. This equation is

$$\frac{\epsilon' - 1}{\epsilon' + 2} \cdot \frac{M}{\rho} = \frac{4\pi}{3} \cdot N\alpha \quad (1)$$

where ϵ' is the dielectric constant, N is Avogadro's number, 6.024×10^{23} , M is the molecular weight, ρ is the density, and α is the molecular polarizability. α is usually discussed in two parts as

$$\alpha = \alpha_e + \alpha_d \quad (2)$$

where α_e is the electronic polarizability which is not temperature dependent and α_d is the polarizability due to orientation of permanent electrical dipole moments. According to a calculation of Debye^{7, 8}

$$\alpha_d = \frac{\mu^2}{3kT} \quad (3)$$

where μ is the dipole moment, k is Boltzmann's constant, 1.38×10^{-16} ergs/°K., and T is the temperature in degrees Kelvin.

In polythene the dipolar polarization might arise from three sources, CH bond moments, C=C bond moments, and impurity moments. The CH moments are small and because of the molecular arrangement cancel completely, e.g. all paraffin hydrocarbon molecules tested have been found to have zero electric dipole moments.⁹ The double bonds may render the molecules somewhat polar but such moments are small (~ 0.3 Debye units) and will certainly be present in small concentration.⁹ Impurity moments will be discussed in a later section but it may be remarked that in ordinary electrical quality polythene they will make a negligible contribution to the dielectric constant.

Therefore it is assumed that $\alpha_d = 0$ or, in other words, that all the polarization is electronic. A test of this assumption is afforded by the comparison of ϵ' and n^2 , the square of the refractive index. According to the Maxwell relation $\epsilon' = n^2$ if ϵ' and n^2 are measured at the same frequency. However ϵ' should be independent of frequency if the polarization is all electronic and the Maxwell relation should hold. Experimentally at 25°C one finds¹² that $\epsilon' = 2.29 \pm 0.01$ and that³ $n_D^2 = 2.295$ supporting the suggestion that $\alpha_d = 0$.

Temperature dependence of the dielectric constant

The temperature dependence of the dielectric constant of polythene has been published by Hahn, Macht, and Fletcher¹³ in the form of a graph. The measurements were made at a constant frequency of

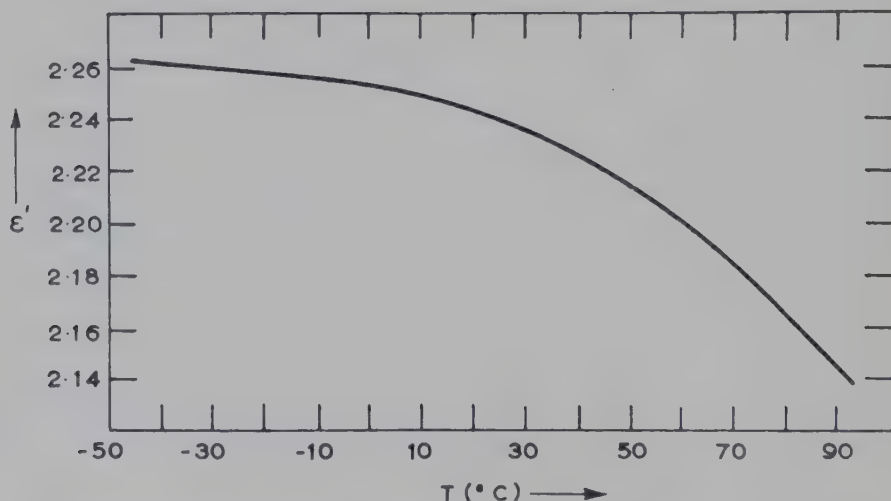


Fig. 8.1. Temperature dependence of the dielectric constant of polythene. (After Shackleton)

3 Mc/sec as revealed by Shackleton¹⁴ who reported the same data. The data are plotted in Fig. 8.1. These data are of unknown accuracy but are in approximate agreement with temperature dependences reported elsewhere.

To investigate the validity of the Clausius-Mosotti equation $(\epsilon' - 1)/(\epsilon' + 2)$ and 0.316ρ are tabulated in Table 8.1. If the Clausius-Mosotti relation holds these quantities should be equal at any temperature. The data of Hahn, Macht, and Fletcher¹³ were used in preparing Table 8.1.

DIELECTRIC PROPERTIES

Table 8.1

T(°C)	$(\epsilon' - 1)/(\epsilon' + 2)$	0.3160
0	0.295	0.296
25	0.293	0.292
50	0.289	0.287
75	0.282	0.279
100	0.274	0.268

The factor 0.316 was found by fitting at 20°C. The agreement is seen to be fairly good but this is not a particularly sensitive test for the equation.

Jackson and Forsyth report that the dielectric constant of polythene is 2.3 at 20°C and 2.15 at 100°C.¹⁵

Von Hippel¹⁶ reports no change in dielectric constant between 24°C and 80°C in one sample of polythene, a finding the present author finds difficult to believe in view of the known density change.

Frequency dependence of the dielectric constant

The assumed non-polar structure of polythene leads one to the conclusion that the dielectric constant will be frequency independent. This prediction is borne out by the observations of Shackleton,¹⁴ which show the value to be 2.3 from 10² to 10⁸ cycles/second. Von Hippel¹⁶ shows values of 2.25 and 2.26, for two different samples, from 10² to 10¹⁰ cycles/second. At 80°C von Hippel reports that the dielectric constant is 2.25 at 3 × 10⁹ cycles/second and 2.20 at 1 × 10¹⁰ cycles/second. In view of what is known about polythene the present author suggests that this dispersion is probably not real. Hunter and Oakes¹⁷ have given 2.3 as the value at 20°C for 50 to 2 × 10⁹ cycles/second and 2.15 for 70°C over the same frequency range. These values are also quoted by Freeth.¹⁸ Jackson and Forsyth¹⁵ report that the dielectric constant is 2.3 at 20°C and 2.15 at 100°C, both values being independent of frequency over the range 50 to 2 × 10⁹ cycles/second.

The pressure dependence of the dielectric constant

The pressure dependence of the dielectric constant has been investigated by the author.¹⁹ Making use of Equation 1 and assuming the polarizability, α , to be a constant, one obtains by differentiation with respect to pressure

$$\frac{1}{\epsilon'} \cdot \frac{\partial \epsilon'}{\partial p} = \frac{(\epsilon' - 1)(\epsilon' + 2)}{3\epsilon'} \cdot \frac{1}{\rho} \cdot \frac{\partial \rho}{\partial P} \quad (4)$$

The volume compressibility may be written

$$K \equiv -\frac{1}{v} \cdot \frac{\partial v}{\partial P} = \frac{1}{\rho} \times \frac{\partial \rho}{\partial P} \quad (5)$$

where ρ is the density. Combining Equations 4 and 5 one obtains

$$\frac{1}{\epsilon'} \cdot \frac{\partial \epsilon'}{\partial P} = \frac{(\epsilon' - 1)(\epsilon' + 2)}{3\epsilon'} \cdot K \quad (6)$$

As ϵ' does not vary by a large amount one may calculate the pressure coefficient of the dielectric constant from Equation 6 using ϵ' determined at atmospheric pressure. Taking $K = 2.5 \times 10^{-5}/\text{atmosphere}$ from Weir²⁰ (extrapolated to low pressure) and $\epsilon' = 2.28$

$$\frac{1}{\epsilon'} \cdot \frac{\partial \epsilon'}{\partial P} = 2.0 \times 10^{-5}/\text{atmosphere}$$

in the low pressure range ($< 1,000$ atmospheres). The measured value up to a few hundred atmospheres is $2.3 \times 10^{-5}/\text{atmospheres}$, but owing to relatively large corrections which must be applied because of pressure-induced geometrical changes in the test condenser the value may be taken to represent agreement.¹⁹

Fig. 8.2 shows the expected pressure dependence of the dielectric constant based on Weir's data and Equation 1. The variation is seen

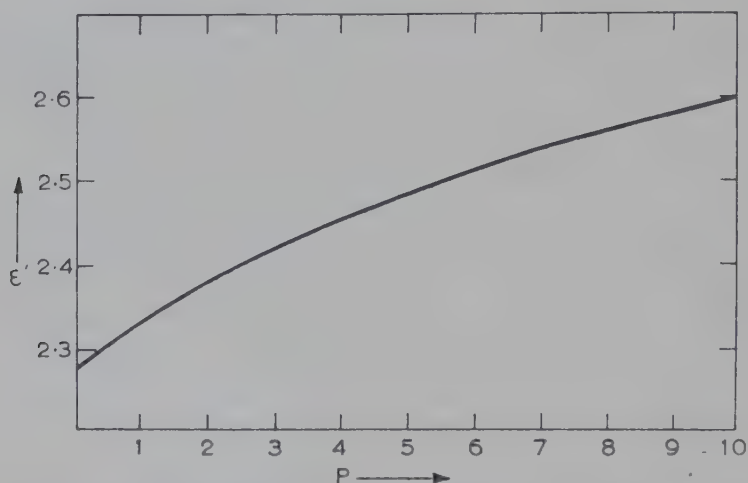


Fig. 8.2. Variation of the dielectric constant with pressure according to Equation 1. The pressure is given in units of 1,000 atmospheres

to be slight even over the extreme pressure range plotted. Furthermore the assumption of constant polarizability probably introduces serious errors at such pressures.^{21, 22} One would expect the polarizability to decrease with pressure and thus the variation of the dielectric constant to be smaller than shown in Fig. 8.2.

Summary on the dielectric constant

The foregoing discussion makes it apparent that in so far as the dielectric constant is concerned polythene behaves as an ideal, non-polar dielectric. The values stated for the dielectric constant in the literature are of uncertain accuracy and the literature is nearly devoid of statements regarding probable errors. Thus, in view of the difficulties encountered

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in measuring the dimensions of soft solids, it would seem advisable to assume the reported values are not known to better than ± 2 or 3 %. The only estimate of error which the present author has uncovered was given by Smith¹² who gave the value 2.29 ± 0.01 at 20°C. The present author has made a number of measurements which are in agreement with those of Smith.

THE DIELECTRIC LOSS

The discussions of the dielectric constant and structure in the preceding sections revealed that polythene exhibits no dispersion of the dielectric constant and polythene is non-polar. Both these facts indicate that polythene will exhibit no dielectric loss over the range of experimental conditions. Experimentally one finds that polythene nearly comes up to this expectation, and its loss is as low as that of any other insulating material known. However there is still a measurable loss ($\tan \delta$) in polythene which changes very slowly with variations in temperature and pressure.*

The dielectric loss is always more sensitive to small concentrations of polar groups than is the dielectric constant and hence a concentration which was negligible in the previous section is responsible for the total effect to be discussed in the present section. The dielectric loss observed in polythene is the result of relaxation of the polar impurity groups which seem always to be present. Debye's theory of the dielectric loss of dilute solutions of polar molecules in a non-polar solvent will form the basis of the discussion.^{23, 24, 25, 26}

It has long been known that polar molecules are often free to rotate even though they are contained in or form part of a rigid lattice.²⁷ Such behaviour is to be expected in polythene where the intermolecular forces are weak and particularly where an appreciable portion of the structure is amorphous. Fig. 8.3 illustrates the manner in which a carbonyl group might fit into the crystal lattice. Note that the carbonyl group has two possible equilibrium positions, i.e. the position shown and the position with the carbonyl group rotated 180° about the chain axis. The activation energy for this rotation will be referred to herein as V .

Consider now a solution of N_2 dipolar groups per cm^3 , each having polarizability $\alpha_2 + (\mu_2^2/3kT)$ in a solvent composed of N_1 CH_2 "molecules", each having polarizability α_1 . Here μ_2 is the dipole moment of the polar groups, k is Boltzmann's constant, and T is the absolute temperature.

The high frequency polarization is

$$P_\infty = (4\pi/3)(N_1\alpha_1 + N_2\alpha_2) \quad (7)$$

* The order of magnitude of $\tan \delta$ is 10^{-4} which is near the lower limit of ordinary methods of measurement. Thus values reported for $\tan \delta$ in good grades of polythene are likely to be subject to large percentage errors.

and the low frequency polarization is

$$P_s = P_\infty + (4\pi/3)(N_2\mu_2^2/3kT). \quad (8)$$

These quantities are related to the complex polarization P by

$$P \equiv \frac{\epsilon - 1}{\epsilon + 2} = P_\infty + \frac{P_s - P_\infty}{1 + j\omega\tau} \quad (9)$$

where $\epsilon = \epsilon' - j\epsilon''$, ω is 2π times the frequency ν , τ is the relaxation time, and $j = \sqrt{-1}$, ϵ' is simply the real dielectric constant treated above, ϵ'' is related to the dielectric loss by $\tan \delta = \epsilon''/\epsilon'$.^{*} Separating the real and imaginary parts of Equation 9 and making use of $\epsilon''^2 \ll \epsilon'^2$ one obtains

$$\tan \delta = \frac{(\epsilon' + 2)^2}{\epsilon'} \frac{4\pi N_2 \mu_2^2}{27 kT} \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (10)$$

and

$$\frac{\epsilon' - 1}{\epsilon' + 2} = \left(\frac{4\pi}{3}\right)(N_1 \alpha_1 + N_2 \alpha_2) + \left(\frac{4\pi}{3}\right) \frac{N_2 \mu_2^2}{3 kT} \frac{1}{1 + \omega^2\tau^2} \quad (11)$$

For small N_2 Equation 11 reduces to Equation 1 as expected.

These equations have been derived upon the assumption of a single relaxation time τ whereas one almost invariably encounters a distribution of relaxation times in practice. Therefore we assume now that the distribution function for relaxation times $G(\tau)$ is defined by^{28, 29}

$$\int_0^\infty G(\tau) d\tau = 1 \quad (12)$$

and

$$G(\tau) d\tau = (Ab/\pi^{1/2}) \exp(-b^2 z^2) dz \quad (13)$$

where A and b are constants. A is defined by the normalization condition, Equation 12, and b indicates the width of the distribution. $z \equiv \ln(\tau/\tau_0)$ where τ_0 is the most probable relaxation time. Equation 10 may now be written as

$$\tan \delta = \frac{(\epsilon' + 2)^2}{\epsilon'} \frac{4\pi N_2 \mu_2^2}{27kT} \int_0^\infty \frac{\omega \tau G(\tau)}{1 + \omega^2 \tau^2} d\tau \quad (14)$$

The distribution of Equation 13 is known²⁹ to hold for a wide variety of systems but it must be emphasized that only one type of polar group has been considered here. Such an absorption (Equation 14) will result from each dipolar group and the observed dielectric loss will be the sum of contributions of the individual groups. In polythene one

* $\tan \delta$ is frequently called D , the dissipation factor.

has the further complication of the crystalline-amorphous composite nature of the system. For example, rotation of a carbonyl group might yield two absorption regions, one for the crystalline region and one for the amorphous region.

Fig. 8.4 illustrates $\tan \delta - \log \nu$ curves for various values of the distribution constant b . Equation 10 is the limiting case of Equation 14 for $b = \infty$. It is noted that the maximum value of the dielectric loss, $\tan \delta_m$, decreases as the distribution broadens. This is related to the fact that the area under a $\tan \delta - \log \nu$ curve is given by³⁴

$$\text{Area} = [(\epsilon' + 2)^2/\epsilon'] [2\pi^2 N_2 \mu_2^2 / 27 kT] \log e. \quad (15)$$

(e is the base of natural logarithms). This result was obtained by Sillars and is independent of the functional form chosen for the distribution of relaxation times. The most probable relaxation time is given by

$$\tau_0 = 1/\omega_m \quad (16)$$

where ω_m is the angular frequency for which $\tan \delta$ is maximized.

The temperature dependence of τ in Equation 10 or τ_0 in Equation 14 is most simply approached by treating τ as an inverse rate of rotation of the dipoles and applying the theory of absolute reaction rates.^{30, 31}

$$\tau = (h/kT) \exp(-\Delta S^\ddagger/k) \exp(\Delta H^\ddagger/kT) \quad (17)$$

where h is Planck's constant, and ΔS^\ddagger and ΔH^\ddagger are the entropy and enthalpy of activation per molecule. Assuming³¹ a potential energy function of the form $(V/2)\cos 2\phi$ for dipolar rotation one finds $\Delta H^\ddagger = V$ and $\Delta S^\ddagger = k \ln 2$. Thus

$$\tau = (h/2kT) \exp(V/kT) \quad (18)$$

This relation may now be introduced into Equation 10 and the temperature dependence of $\tan \delta$ thus derived. Use of Equation 18 in Equation 14 is difficult because the integral in Equation 14 has been evaluated only numerically. It is not profitable in any case as the temperature dependence of the parameter b is unknown.

The important conclusions to be gained from the foregoing theory are as follows:

- (1) $\tan \delta$ increases as $N_2 \mu_2^2$,
- (2) $\tan \delta$ is maximized for $\omega\tau = 1$ and falls to zero with increasing or decreasing frequency.
- (3) $\tan \delta$ depends upon temperature in two ways
 - (a) through the exponential dependence of τ upon T , which results in a dependence rather like the frequency dependence, Equation 18,

- (b) through the inverse temperature relation which results in $\tan \delta_m$ varying as $(1/T)$, Equation 14,
- (4) $\tan \delta$ depends upon the potential barrier to rotation through the exponential dependence of τ on V , i.e., ν_m , the frequency of maximum loss, decreases with increasing V .

Frohlich³² has worked out a detailed theory for the calculation of V based upon a structural model. He attributes a certain amount of torsional flexibility to the long chain molecules and proceeds to derive the dependence of V upon chain length. This theory is in good agreement with experiment for solutions of long chain esters in paraffin wax and thus has obvious applications here.^{33, 34, 35}

Experimentally the dielectric loss in polythene has been studied many times. Von Hippel¹¹ reports that $\tan \delta < 2 \times 10^{-4}$ from 10^2 to 10^7 cycles/second and is 3.1×10^{-4} and 3.6×10^{-4} at 3×10^9 and 10^{10} cycles/second. These results were obtained on one sample at 25°C . On another sample values of 7.2×10^{-4} and 8.5×10^{-4} were found at 3×10^9 and 10^{10} cycles/second at 80°C . This sample showed higher losses than the first at 24°C .

Shackleton¹⁴ reports that $\tan \delta$ rises linearly with $\log \nu$ between 10^2 and 10^8 cycles/second going from 1×10^{-4} to 2×10^{-4} . Shackleton also reports the temperature dependence which shows a broad maximum of 2.5×10^{-4} for 3×10^6 cycles/second near room temperature.

Jackson and Forsyth¹⁵ give the temperature dependence of $\tan \delta$ from -80 to $+80^\circ\text{C}$. Over this range $\tan \delta$ rises from 1×10^{-4} to 5×10^{-4} at 2×10^9 cycles/second. Jackson and Forsyth also report that $\tan \delta$ is almost independent of frequency from 10^5 to 2×10^9 cycles/second. Hunter and Oakes¹⁷ give similar data.

Oakes and Robinson³⁶ report that they have made low frequency precision measurements on low loss polythene as a function of temperature and have established the existence of three overlapping loss peaks.

The observed loss data may be satisfactorily explained by assuming that there are a variety of polar groups in polythene, each present in low concentration and each contributing a broad, weak loss maximum. It may easily be demonstrated that the sum of three fairly broad loss curves is practically linear over an enormous frequency range.³⁷

Additional experimental evidence in favour of the above explanation is presented in the next section concerning the effects of introducing polar materials into polythene. The infra-red spectrum does identify carbonyl and hydroxyl groups as the major impurities with carboxyl and hydroperoxide groups also present.^{38, 39, 40} It should be mentioned, however, that a detailed description of the nature of the polar groups and their environs cannot be given at this time.

THE EFFECTS OF POLARITY ON POLYTHENE

As indicated in the preceding section, there is good evidence that ordinary polythene contains small concentrations of polar groups. These groups can enter the polymer either during polymerization or after the

material is in use. This section will be devoted to the consideration of a few of the possible polar constituents.

The effects of chemically combined carbon monoxide

Jackson and Forsyth^{15, 41} have studied a polythene prepared from ethylene which contained small quantities of carbon monoxide. These authors demonstrate that the concentration of [CO] in the polymer is about fifteen times higher than the concentration in the gas mixture. As an example of the magnitude of this effect, addition of 0.4% by weight carbon monoxide in ethylene results in a polymer containing about 6% [CO] by weight, and the polymer exhibits a dielectric loss of about 250×10^{-4} , an increase by a factor of about 100 over the pure material. $\tan \delta$ increases linearly with carbon monoxide concentration

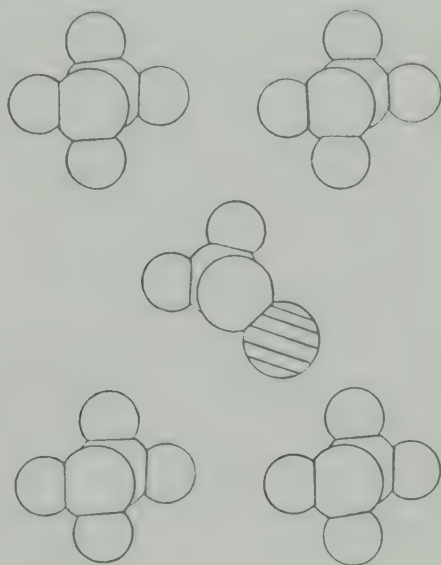


Fig. 8.3. The arrangement of the zigzag carbon chains with a carbonyl group replacing a methylene group. The oxygen atom is cross-hatched. The circles are not intended to represent relative atomic sizes

over the range studied (up to about 8% by weight in the polymer) as predicted by Equations 10 and 14.

Jackson and Forsyth, on the basis of X-ray data, suggest that the carbon monoxide is copolymerized with the ethylene and becomes carbonyl in the chain. (See Fig. 8.3.)

$\tan \delta$ was measured as a function of frequency for a polymer containing 0.4% [CO] by weight. $\tan \delta$ was observed to pass through a maximum of about 30×10^{-4} between 10^8 and 10^9 cycles per second and fell to 10×10^{-4} at 10^5 cycles per second. This slow variation is indicative of a very broad distribution of relaxation times. Jackson and Forsyth estimated the area under the $\tan \delta - \log \nu$ curve and employed the relation of Sillars,³⁴ Equation 15, to estimate the concentration of carbonyl. The concentration calculated in this way is in fair agreement with the concentration obtained by chemical means.

Jackson and Forsyth also reported measurements on a commercial sample of polythene which showed a maximum of about 2.7×10^{-4}

in the $\tan \delta - \log \nu$ curve at about 2×10^9 cycles/second. Assuming that this peak is due to [CO] groups and applying Equation 15, they estimate that the [CO] concentration in the polymer was about 0.03% by weight, corresponding to only 0.002% by weight of carbon monoxide

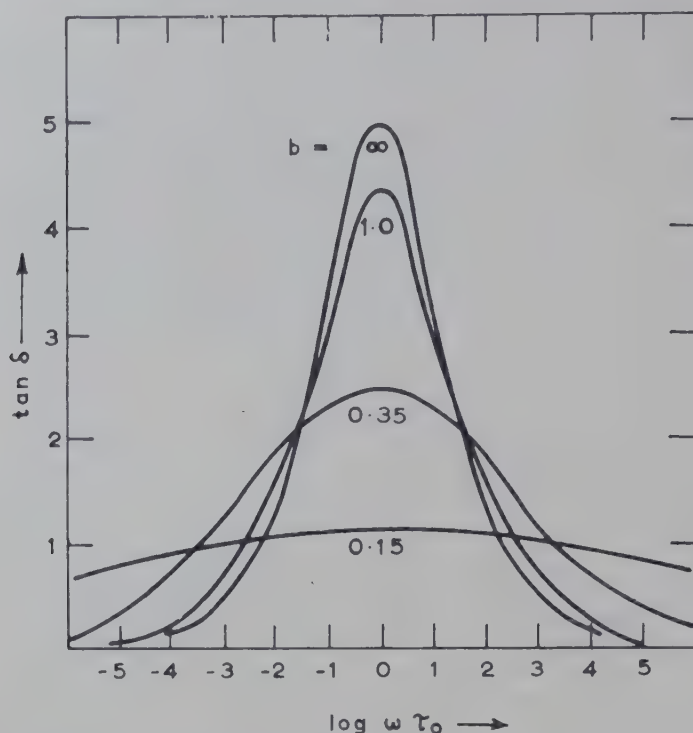


Fig. 8.4. $\tan \delta$ (in arbitrary units) plotted against $\log \omega \tau_0$ showing the effect of a broadened distribution of relaxation times on the form of the curve

in the initial ethylene. Though this result is not conclusive it is very strong evidence that the basic loss in polythene is primarily the result of carbonyl relaxation.

The effects of combined oxygen

Numerous studies have been made on the effects of oxidation on the dielectric properties of polythene. The chemistry of the situation has been discussed by Jackson and Forsyth¹⁵ and reviewed more recently by Biggs.^{42, 43} Oxidation is thought to proceed via a free radical mechanism involving hydroperoxide intermediates, but the final products are probably mainly present in the form of carbonyl, hydroxyl, and carboxyl groups.

Jackson and Forsyth¹⁵ have made observations of the dielectric loss of polythene as a function of frequency and temperature on material which has been milled in the presence of oxygen for several hours at 160°C. The loss increases, at a given frequency, with temperature of milling, time of milling and speed of milling (or degree of mixing). The $\tan \delta - \log \nu$ curves (over the frequency range 10^5 to 2×10^9 cycles per second) indicate a broad distribution of relaxation times. The loss maxima are rather curious in shape and cannot be closely fitted by a distribution such as that given in Equation 13. At room temperature the frequency of maximum loss is near 10^8 cycles/second. The temperature

dependence data are not sufficiently complete to allow an accurate calculation of the rotational energy barrier but a rough estimate of 20 k cal/mole may be obtained. The interpretation of this result is difficult as more than one type of dipolar group is probably present.

The present author has made measurements¹⁹ of the dielectric loss of polythene oxidized in the same manner as the specimens of Jackson and Forsyth. The results agree closely with Jackson and Forsyth but have been carried to lower frequencies (10^3 to 10^8 cycles per second) to investigate the strangely intense tail of the $\tan \delta - \log \nu$ curve. These data are shown in Fig. 8.5 for a sample which had been milled for 2 hours at 150°C . In the same figure, the solid curve is the theoretical

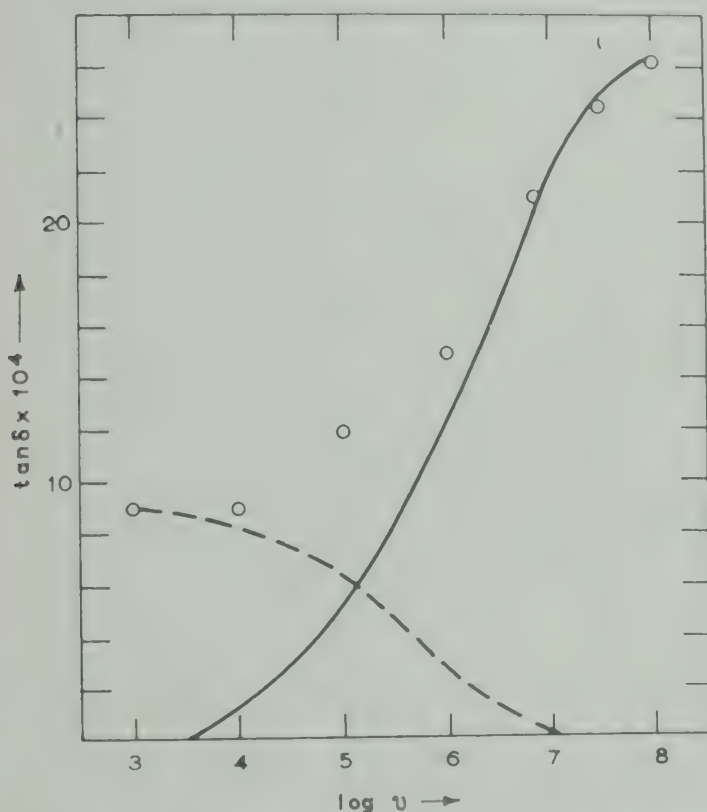


Fig. 8.5. A plot of $\tan \delta$ against $\log \nu$ plot for a commercial polythene which was oxidized for two hours on a mill at elevated temperature. The experimental points are circled. The solid curve is done in the manner of Yager. The dashed curve is the difference

loss curve from Equation 14 by the method of Yager²⁹ and fitted to the experimental points in the higher frequency range. The dashed curve is the difference between the experimental points and the theoretical fit. As the dashed curve has the general shape defined by Equation 14, it may be suggested that a second loss maximum occurs near 10^3 cycles per second.* The two loss peaks could be attributed to the presence of two different polar groups (e.g., carbonyl and hydroxyl) or to a single

* Decomposition of the $\tan \delta - \log \nu$ curve in this manner is a questionable procedure owing to the uncertainty in the validity of Equation 13. Sillars³¹ has demonstrated, however, that such decomposition is valid when two dipolar impurities are added to paraffin wax.

type of polar group present in two distinct environments (e.g., the crystalline and amorphous zones).

Oakes and Robinson³⁶ have recently presented a brief report of an extremely interesting research programme in which they establish the existence of fine structure in the $\tan \delta$ — temperature curve for oxidized polythene. Their results for 1.1×10^4 cycles per second are shown in Fig. 8.6. These authors identify three loss peaks and relate them to loss peaks observed in the temperature dependence of the mechanical

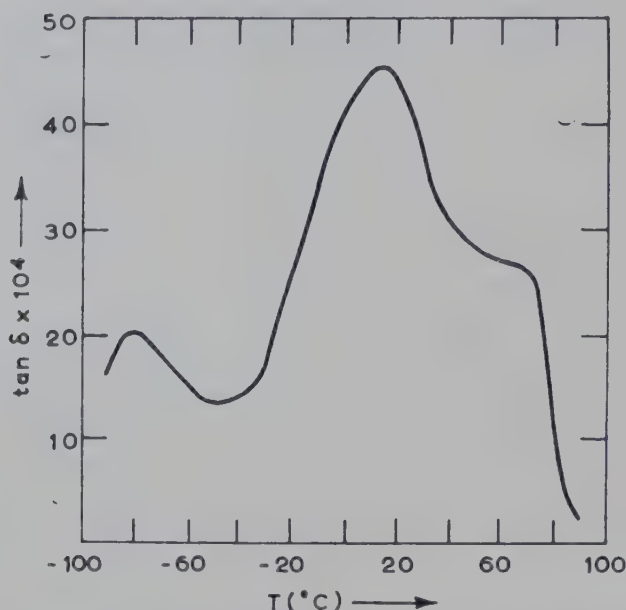


Fig. 8.6. $\tan \delta$ as a function of temperature for oxidized polythene. (After Oakes and Robinson)

loss. Activation energies evaluated from the electrical measurements for the three processes corresponding to the three loss peaks were calculated to be roughly 60, 55 and 13 kcal/mole.

Oakes and Robinson observe that the loss peaks are increased in intensity, but are not shifted in frequency by oxidation. Furthermore, the dispersion region between -60°C and $+40^\circ\text{C}$ is missing for straight-chain polymethylene and they thus attribute this dispersion to side chain activity. Further work of this sort will greatly enrich our knowledge of the molecular motions of these systems.

The effect of oxidation on the dielectric constant and loss has been reported by Biggs⁴² for thermally oxidized material. These results are shown in Figs. 8.7 and 8.8. The upward curvature of Fig. 8.8 and the proportionality between the quantity of oxygen absorbed and $\tan \delta$ demonstrates the autocatalytic nature of the oxidation reaction. Similar results for the dielectric loss have been reported by Hahn, Macht, and Fletcher¹³, and Myers.⁴⁴

Myers showed that $\tan \delta$ at 5×10^7 cycles per second is proportional to carbonyl oxygen concentration supporting the view that the loss peak in this region is the result of carbonyl relaxation.

DIELECTRIC PROPERTIES

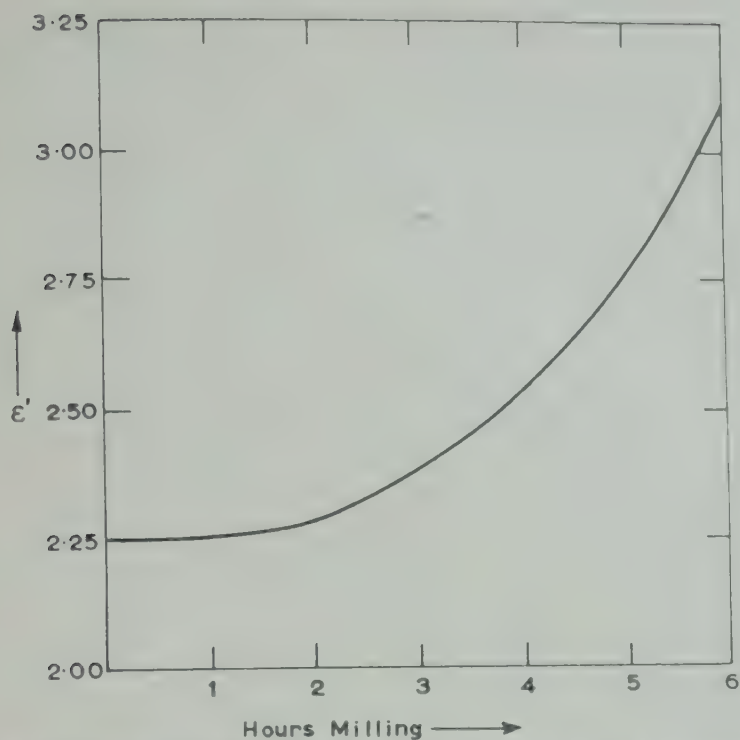


Fig. 8.7. The dielectric constant of polythene as a function of time of oxidation by milling at 160°C . Measurements were made at 5×10^7 cycles/second at room temperature. (After Biggs)

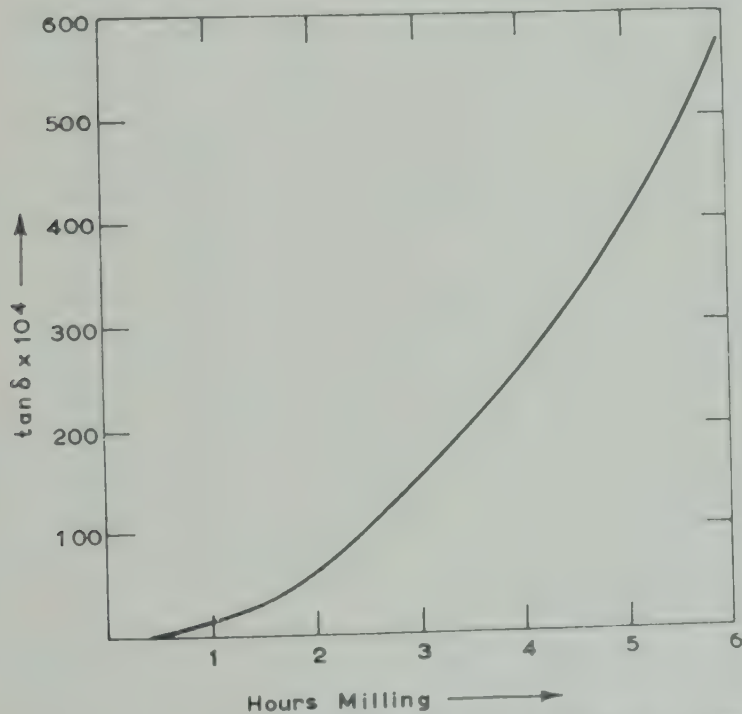


Fig. 8.8. $\tan \delta$ of polythene as a function of time of oxidation by milling at 160°C . Measurements were made at 5×10^7 cycles/second at room temperature. (After Biggs)

Von Hippel¹¹ reported the frequency dependence of the dielectric constant and loss of polythenes which had been milled at 125°C and 190°C for 30 minutes. These measurements cover the range from 10^2 to 10^{10} cycles/second. Both the 125°C and 190°C samples were measured at 23°C and the 190°C sample was also measured at -12°C.

Pross and Black⁴⁵ determined the dielectric loss of polythene as a function of time of irradiation by ultra-violet light. The wave lengths responsible for deterioration lie between 2,900 and 3,300 Å, a region in which carbonyl groups absorb. A mercury arc lamp was used to irradiate the specimens and $\tan \delta$ at 10^3 cycles/second increased from 2×10^{-4} to 12×10^{-4} in 150 hours of irradiation. Pross and Black also showed that the amount of oxygen absorbed is proportional to the dielectric loss measured at 10^3 cycles/second.

The effects of combined chlorine

Oakes and Richards⁴⁶ have studied the dielectric constant and loss of chlorinated polythene as a function of temperature and frequency. Their measurements were made on samples containing 2, 8, 25, 40, 45, 54, and 60% chlorine by weight. The samples were prepared by direct chlorination of the polythene, a fine powder of which was dispersed in carbon tetrachloride.

Loss peaks of about 150×10^{-4} , 400×10^{-4} , and $1,300 \times 10^{-4}$ were observed at about 10^8 , 10^7 , and 10^6 cycles per second for the 2, 8, and 25% samples respectively. The loss peaks for the higher concentration specimens could not be observed as they fell below 10^5 cycles per second, the lower frequency limit of this study. The reason for the decrease in frequency of maximum loss with chlorine concentration is the increased intermolecular forces which result from the increased polarity of the molecules.

Dielectric constants fell between about 4.1 for the 25% specimen at 10^5 cycles per second and 2.4 for the 60% specimen near 10^6 cycles per second, the measurements having been made at 16°C. Dispersion is observed for those samples exhibiting loss peaks in the experimental range. The dielectric constant of the 60% specimen probably increases at a lower frequency or higher temperature. The static dielectric constant will not increase directly as chlorine content, however, as beyond a certain point cancellation of bond moments occurs, leading ultimately to a non-polar polymer, polytetrachloroethylene. At 60% by weight chlorine there are 0.55 chlorines per carbon. Sillars' method³⁴ was used to estimate the "average" dipole moment which was observed to decrease with chlorine content.

Two series of samples were measured, one chlorinated at 65–70°C and the other at 30–40°C. The loss of the cold chlorinated material was lower than that of the hot chlorinated material. The reason given for this observation is that at the higher temperature the chains are more likely to be extended and the chlorine may enter all along the chain. At the lower temperature the chains are more likely to be coiled and the

chlorines have only limited access. This situation results in the chlorine entering the cold chlorinated chains in such a way as to produce a larger cancellation of bond moments.

The effects of esters in solution

Plessner and Richards⁴⁷ have made measurements on a 2% solution of dioctyl phthalate in polythene and measured the dielectric loss over the frequency range 10^4 to 10^8 cycles per second and over the temperature range -33 to 17°C . The $\tan \delta - \log \nu$ curves are generally of the sort predicted by Equation 14 but exhibit a slight asymmetry. The peaks broaden as the temperature is decreased, i.e., the parameter b decreases. The dipole moment calculated from Sillars' relation, Equation 15, is 2.6 Debye units. The activation energy for dipole rotation is found to be 15 kcal/mole, as compared with 28 kcal/mole calculated from the data of Jackson³³ for a solution of cetyl palmitate in paraffin wax. Plessner and Richards suggest that in polythene the esters lie in amorphous regions and encounter smaller barriers to rotation than in the crystalline paraffin wax. The suggestion that the ester molecules lie in the amorphous regions is supported by the fact that Plessner and Richards obtain a value of 16 kcal/mole for a 2% dioctyl phthalate in polyisobutene solution. Polyisobutene is entirely amorphous. Sillars,³⁴ however, has made measurements on cetyl palmitate in paraffin wax (at the same concentration used by Jackson), and activation energies calculated from his data lie close to those found by Plessner and Richards in polythene.

Plessner and Richards also observed the dielectric loss of solutions of other esters in polythene and their results are tabulated in Table 8.2.

Effects of the addition of miscellaneous materials

Water may be present in pure polythene to the concentration of 0.04% but Jackson and Forsyth¹⁵ have shown that the effects on the dielectric properties are negligible.

Antioxidants, such as diphenyl *p*-phenylene diamine, are usually added to polythene to retard oxidative aging of the material.⁴² These substances are added in concentrations of 1% or less and produce no significant effects on the dielectric properties. It may be added that chemical

Table 8.2—VALUES OF $\tan \delta_m$ AND ν_m FOR POLYTHENE-ESTER MIXTURES AT CA. 16°C

Ester	Concentration	$\tan \delta_m$	ν_m
Dibutyl phthalate	0.6%	15×10^{-4}	8×10^7
Dibutyl phthalate	2.0%	48×10^{-4}	10×10^7
Dihexyl phthalate	2.0%	50×10^{-4}	3.5×10^7
Dioctyl phthalate	2.0%	54×10^{-4}	1.3×10^7
Tricresyl phosphate	0.06%	6×10^{-4}	3×10^7
Tricresyl phosphate	2.0%	40×10^{-4}	1.6×10^7
Propyl stearate	6.6%	$>30 \times 10^{-4}$	$>10 \times 10^7$

antioxidants are spectacularly successful in suppressing oxidation and consequent deterioration of electrical properties in polythene.

To protect polythene from the effects of ultraviolet light lead chromate, iron oxide, or carbon black may be added to concentrations of 1 to 2%.* The effects of these materials may be estimated by use of the theory of the Maxwell-Wagner effect.^{9, 10} Sillars' extension⁴⁸ of this "inhomogeneity" theory to describe dispersions of semi-conducting spheres suspended in loss-free dielectric would seem applicable in the low concentration range.

Unfortunately, no experimental studies have been reported to test this theory in polythene. Bostwick and Carey⁴⁹ have observed that $\tan \delta$ of polythene increases from 3×10^{-4} to 90×10^{-4} (at 5×10^7 cycles per second) and ϵ' increases from 2.3 to 2.9 on addition of 40% clay. Ambrose⁵⁰ is currently investigating the effects of various carbon blacks on polythene with special attention given to particle size, degree of dispersion, and concentration effects. Ambrose has found a loss peak in all samples of polythene containing carbon black at 7×10^4 cycles per second. This peak is similar to those observed in carbon black loaded natural rubber, neoprene, butaprene and similar substances as observed by Carter, Magat, Schneider, and Smyth⁵¹ and Dogadkin and Lukomskaya.^{52, 53} These authors propose that the peak is due to the Maxwell-Wagner effect but calculations based on Sillars' equations⁴⁸ and a reasonable conductivity for carbon indicate the frequency of maximum loss should be in the near infra-red.

THE DIELECTRIC STRENGTH

As the voltage across a slab of dielectric is slowly increased, a condition is eventually reached at which the dielectric abruptly becomes a conductor, i.e., breaks down. The electric field at breakdown, E_b , is called the dielectric strength, electric strength, or breakdown strength of the dielectric material. The measurement of the electric strength of a solid is difficult and the effects of voids in the samples, and variations in electrode systems must be carefully eliminated if the data are to be of any value. Fortunately, measurements on polythene are available which are free of such extraneous effects.

Several theories of dielectric strength of solids have been set forth^{54, 55, 56} by von Hippel and Frohlich. Frohlich's theory of electronic breakdown will be used to discuss the effects observed in polythene. Frohlich distinguishes two regions of temperature separated by a critical temperature, T_c , at which the mechanism of breakdown changes. Below T_c the conduction electrons are present in low concentration and collisions between electrons may be neglected. The mean free paths of the electrons may then be relatively long and the external field can accelerate the electrons to high energies. When a sufficient number of electrons have energies greater than the ionization energy of the atoms present, breakdown can occur. The dielectric strength in this region is thus increased

* See Chapter 6.

by the addition of scattering centres to the material which tend to reduce the mean free paths of the electrons and keep their energies low. This may be done by admixture of foreign materials, decreasing crystallinity, or raising the temperature. The temperature effect is slight. Above T_c the electrons are present in the conduction bands in concentrations which are sufficiently high that collisions between conduction electrons predominate over electron-lattice collisions. In this region a different breakdown mechanism operates and breakdown is due to lower energy conduction electrons. The electric strength in the high temperature region is reduced by admixture of foreign materials and by crystalline imperfections, as these provide trapping centres for electrons. Also, the theory shows that, above T_c ,

$$\log E_b \propto \frac{\Delta V}{T} \quad (19)$$

where ΔV is the energy range of the excited levels.

Experimentally, Oakes has made careful measurements which are in qualitative accord with Frohlich's theory. The d.c. electric strength of polythene is shown in Fig. 8.9, the values being those of Oakes.^{57, 58, 59} These values agree with those of Austen and Pelzer⁶⁰ and Bird and Pelzer.⁶¹ The critical temperature appears to be near room temperature and the

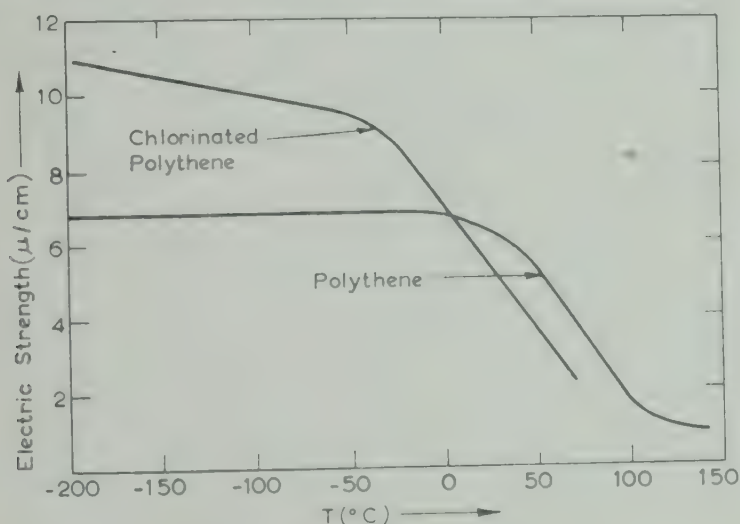


Fig. 8.9. The dielectric strength of polythene and chlorinated polythene (containing 8% chlorine by weight) (After Oakes)

low temperature thermal effect appears to be negligible. The high temperature region of polythene is complicated somewhat by the fact that the degree of crystallinity of the polythene varies with temperature. The dielectric strength of a chlorinated sample of polythene⁵⁹ is also shown in Fig. 8.9. The increase in low temperature strength and decrease in high temperature strength are predicted by Frohlich's theory, as is the depression of the critical temperature. The critical temperature of polyisobutene is near -60°C , due to its highly amorphous structure.⁵⁹

Oakes' work also supports another conclusion from Frohlich's theory. That is, that the electric strength is independent of specimen thickness (unless the thickness becomes comparable with the electronic mean free path).

A.c. breakdown tests have been made by Oakes⁵⁷ and Riddlestone.⁶² The results are more disperse and the strengths observed are lower than obtained by d.c. measurements. This is thought to be due to local internal heating at inclusions of impurities.

EFFECTS OF STRUCTURE VARIATIONS

The preceding sections have been concerned with the description of ordinary commercial polythene prepared from ethylene gas by polymerization at high temperatures and pressures. Such material is branched such that it is usually about 40–50% amorphous. Recently, other polythenes have been made available which differ in preparation and properties from those discussed herein.⁶³ The differences in properties may be explained by simple structural considerations. (See Chapter 7).

The three types of polythene may be characterized by their preparations. Polymethylene, a straight CH_2 chain, may be synthesized by the decomposition of diazomethane. The degree of crystallinity of this material is about 95%. Less crystalline polythenes may be obtained by catalytic polymerization of ethylene at moderate conditions of temperature and pressure. Non-crystalline but highly cross-linked polythene may be obtained by exposure of ordinary polythene to ionizing radiations. (See Chapter 13).

Generally, as the polymers become more linear they increase in crystallinity and become more dense,⁶⁴ and their dielectric constant increases as Equation 1 predicts. The dielectric loss depends upon the impurity content and is not expected to be affected by the crystallinity (however, see reference 36). The dielectric strength, according to Frohlich's theory, should be lower below T_c but higher above T_c for more crystalline materials. T_c should increase with crystallinity.

The density dependence may be deduced from Equation 1 by differentiation and use of $\epsilon' = 2.29$ when $\rho = 0.92$. This yields

$$\epsilon'(\rho) = 2.29 + 2.0(\rho - 0.92) \quad (20)$$

an approximate relation. The dielectric constant of polyisobutene should be low as it represents an almost entirely amorphous $(\text{CH}_2)_n$ polymer.

Some data on the high density polythenes are assembled in Table 8.3. The data refer to room temperature. The Ziegler material mentioned in Table 8.3 shows evidence of the presence of residual catalyst.

Baccaredda and Schiavinato have studied the refractive index of polythene as a function of chain branching.⁶⁷ Their results indicate a

DIELECTRIC PROPERTIES

Table 8.3—DIELECTRIC PROPERTIES OF SOME HIGH DENSITY POLYTHENES

	Ziegler ⁶⁵	Marlex ⁶⁵	Polymethylene ^{64, 66}
Density	0.95	0.96	0.98
Dielectric constant	2.37	2.35	2.38
Dielectric loss—			
10 ⁴ cps	32 × 10 ⁻⁴	1-3 × 10 ⁻⁴	
3 × 10 ⁷ cps	16 × 10 ⁻⁴	1-3 × 10 ⁻⁴	
60 cps			8 × 10 ⁻⁴
3 × 10 ² cps			3 × 10 ⁻⁴
10 ³ cps			1 × 10 ⁻⁴

general trend of increasing density and refractive index with increasing CH₂/CH₃ ratio.

Goodwin⁶⁸ has described a polythene prepared by exposing ordinary polythene to 100 Mev electrons. A highly cross-linked material results for which Goodwin reports $\epsilon' = 2.3$ and $\tan \delta < 5 \times 10^{-4}$, presumably at room temperature. It is to be supposed that oxygen must be excluded if the dielectric properties are to be preserved.

The effect of varying the spherulite^{2, 3} size has not been demonstrated nor has it been shown whether orientation of the molecules affects the dielectric constant and loss in polythene. Oriented polythene does show a slight optical birefringence, however.³

ACKNOWLEDGMENT

The author wishes to acknowledge the aid of W. O. Baker, W. P. Slichter, G. T. Kohman, and D. B. Herrmann in the preparation of this chapter.

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CHAPTER 9

GENERAL MECHANICAL PROPERTIES

A. H. WILLBOURN

POLYTHENE is the generic name for the family of high molecular weight polymers made by the polymerization of ethylene. Different conditions of synthesis lead to products which differ in molecular weight and molecular weight distribution, and in the number and length of chain branches; these differences on the molecular scale result in a wide range of physical properties as is illustrated^{1, 2} qualitatively up to moderately high molecular weights in Fig. 9.1. The characteristic toughness and flexibility of polythene is associated with polymers of high molecular weight; it is these polymers which are useful as plastics. The mechanical properties of these polymers also depend on the extent to which the

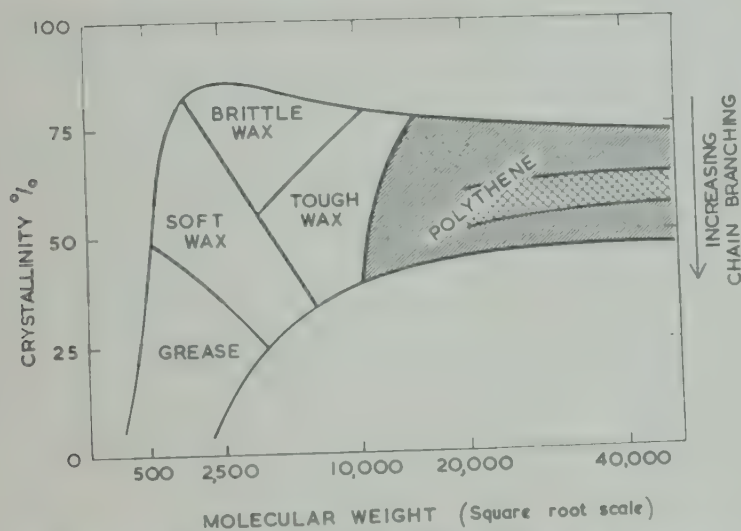


Fig. 9.1. The relation between molecular weight, crystallinity and physical properties of ethylene polymers

molecules are branched, since this controls the degree of crystallinity of the polythene. High density, high crystalline melting point and hardness go with high crystallinity; within the shaded area of Fig. 9.1 lie polythenes with densities ranging from about 0.90 to 0.94 gm/cc and melting points from 105° to over 120°C. Polythenes in general use do not show such a wide spread of properties; they fall roughly in the hatched region shown in Fig. 9.1, with densities around 0.92 gm/cc and crystalline melting points of about 110°–115°C.

High molecular weight polymers of the same stoichiometric formula as polythene, viz. $(\text{CH}_2)_n$, but with essentially linear unbranched mole-

cules, were prepared in 1948 by Leitch and Cambron³ and have been made and examined since by many workers.^{4, 5, 6, 7, 8} These "polymethylenes" are highly crystalline; they have densities in the region 0.95 to 0.98 gm/cc and crystalline melting points 130°–140°C. Polymers of ethylene have recently been marketed with properties similar to the above mentioned polymethylenes. The present state of knowledge on these materials is reviewed in a later section of this chapter.

GENERAL CONSIDERATIONS

Although polythene is only moderately strong, with a tensile strength in the region of 2,000 lb/sq. in., its toughness and extensibility make it suitable for use in the form of film down to a thickness of a few thousandths of an inch; it is insoluble in all solvents at temperatures below 60°C, though swollen by some, and retains its flexibility down to below – 100°C; it can be drawn into filaments with tensile strengths in the region of 20,000 lb/sq. in.

Structure and properties

The properties of polythene are best understood and related to each other through an understanding of its structure and "texture", i.e. in terms not only of the sizes and shapes of the molecules, but also of the manner in which they are organized in the amorphous and crystalline regions.* The individual crystallites have dimensions of the order of a few hundred Ångströms, much less than the wavelength of visible light, and do not themselves therefore produce opacity. However, they are normally organized in spherulitic aggregates, much larger than the wavelength of light, and it is these which render polythene opaque in thick sections. The overall degree of crystallinity is controlled by the number of branches in the polymer chains. Depending then on the structure of the molecules, the crystallites usually occupy some 50–75% of the volume, and they act as "reinforcing units" embedded in an amorphous matrix, the whole being tied together by the long molecules which meander from crystallite to crystallite through the amorphous regions.

The crystallites melt over a wide range of temperature, but melting does not occur to any appreciable extent below about 50° to 60°C.^{1, 9} Above this temperature the mechanical properties of polythene deteriorate at a rapidly increasing rate due to the melting of crystallites, whereas at lower temperatures changes in mechanical behaviour are dominated by the behaviour of the amorphous regions. The available evidence indicates that the $(\text{CH}_2)_n$ chain is inherently fairly flexible and that segmental motion can occur down to temperatures below – 100°C, i.e. that the "glass transition" temperature, T_g ¹⁰, is below – 100°C. The fact that polythene can show rubber-like behaviour has recently been demonstrated

* See Chapter 7.

using materials cross-linked and rendered almost amorphous by high energy radiation.* Polythene may therefore be looked upon as a flexible plastic material, "self-reinforced" by crystallites. Broadly speaking, those properties which involve only small deformations are dependent on its degree of crystallinity, and hence show a correlation with density, whereas properties involving large deformations, and in particular fracture, depend more on molecular weight.^{2,11} This is exemplified in Table 9.1.

Table. 9.1

Properties mainly dependent on degree of crystallinity	Properties mainly dependent on molecular weight
Melting and softening point Surface hardness Elastic modulus Stress and strain at yield point	Ultimate tensile strength Elongation at fracture Low temperature brittle point

Molten polythene: melt flow index and molecular weight

Above its crystalline melting point polythene becomes a very viscous liquid showing markedly non-Newtonian behaviour. Despite this fact, it has been found that its melt viscosity, measured under standard conditions, correlates approximately with its number average molecular weight, \bar{M}_n , and is one useful criterion for characterizing polythenes for different applications. Conventionally the fluidity of molten polythene is determined at 190°C using an extrusion plastometer of standard design, and expressed in arbitrary units as the "melt flow index" (M.F.I.)¹². The M.F.I. is simply related to the apparent viscosity η^* , by the approximate relation:—

$$\eta^* \text{ (poise)} = \frac{7.5 \times 10^4}{\text{M.F.I.}} \quad (1)$$

The viscosity is derived by simple theory from the known dimensions of the plastometer. The correlation with molecular weight takes the form of a logarithmic dependence of viscosity on the square root of the *number average* molecular weight, \bar{M}_n , and is given by Equation 2.

$$\log \eta^* = A + B (\bar{M}_n)^{\frac{1}{2}} \quad (2)$$

This is an empirical correlation of a rather unexpected form which will be discussed further. It does not apply to polythenes of widely different structures, and indeed one would expect the behaviour of molten polythene to depend on the number and sizes of branches in the molecules. However, for low density polythenes it is a reasonable approximation. This is shown by the data presented in Table 9.2, where values of \bar{M}_n computed

* See Chapter 13.

from osmotic pressure measurements are compared with values derived from measurements of melt fluidity, combining Equations 1 and 2 the form of Equation 3:¹³

$$(\bar{M}_n)^{\frac{1}{2}} = 188 - 30 \log (\text{M.F.I.})$$

it will be noted that as the dependence of viscosity on molecular weight is logarithmic, quite small changes in \bar{M}_n result in large changes in η and M.F.I.; for a change in \bar{M}_n of less than 3 : 1, M.F.I. changes by a factor of 30,000. This method of characterizing polythene with respect to molecular weight is, therefore, a very sensitive one, and a high degree of accuracy in measurement is not called for.

Table 9.2—THE RELATIONSHIP BETWEEN MELT VISCOSITY AND MOLECULAR WEIGHT

M.F.I.	η *poise at 190°C ^a	\bar{M}_n (calc. ^b)	\bar{M}_n (exp.) ^c
170	450	15,000	19,000
70	1,100	18,000	21,000
21	3,600	22,000	24,000
6.4	12,000	27,000	28,000
1.8	42,000	32,000	32,000
0.25	3×10^5	42,000	48,000
0.005	1.5×10	66,000	53,000

(a) Calculated from the M.F.I. using Equation 1.

(b) Calculated from the M.F.I. using Equation 3.

(c) Determined from osmotic pressure measurements in xylene at 85°C.

The effect of additives

Since polythene is tough and flexible there is little to be gained by attempting to plasticise it, even if its solubility characteristics permitted this to be done. It has, however, sometimes been found advantageous to blend relatively low molecular weight polythenes ($\bar{M}_n \lesssim 25,000$, M.F.I. $\gtrsim 20$) with minor amounts of polyisobutylene to enhance certain properties. For the most part, polythene is used in its natural state, admixed only with small proportions of organic or inorganic materials which act as stabilizers or colourants; their effects on the mechanical properties of polythene and on its behaviour in the molten state may be ignored.

PROPERTIES IN TENSION

A general description of the way in which the mechanical properties of polythene are dependent on its molecular weight and degree of crystallinity has been given above.

Form of the stress-strain curve

The type of stress-strain curve obtained on a high molecular weight polythene is shown schematically in Fig. 9.2. The portion of the curve OA from the origin to the yield point A, covers the total useful range of

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stress and strain for most applications. Strains up to the strain at the yield point are fully recoverable, given sufficient time; it appears that there is no irreversible change in the spherulitic "texture" of the polymer, the strain being taken up by reversible deformations in the amorphous regions.

At higher strains, "cold drawing" takes place. A neck usually develops and the specimen elongates some four to six times, without much increase in the force necessary to produce this elongation, until at *B* a natural limit is reached leaving a specimen of uniform, but smaller, cross-section. Cold drawing is a phenomenon shown by many high polymers and is not peculiar to the crystalline ones. It arises from the adiabatic nature of

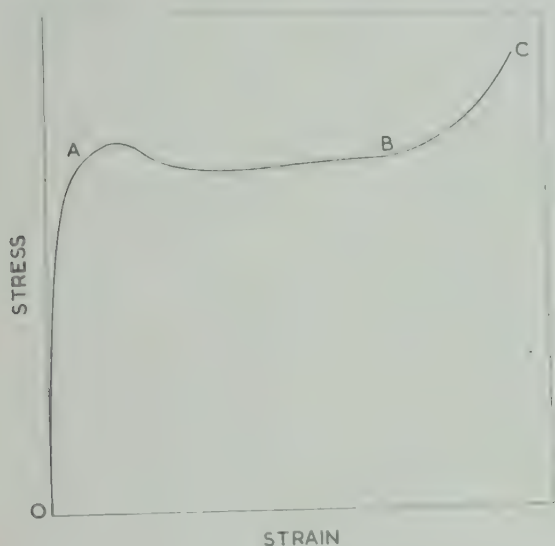


Fig. 9.2. Stress-strain curve for polythene (schematic)

A: yield point
AB: region of "drawing"
C: point of fracture

the extension process and a particular dependence of modulus on temperature; the detailed behaviour of any particular specimen is a function of its geometry, the temperature and rate of extension. The process has been discussed and reviewed by Marshall and Thompson.¹⁴ Crystalline polymers such as polythene show detailed differences in behaviour from amorphous ones because the drawing process must involve the breaking down of the original spherulitic aggregates of crystallites. The re-ordering of the crystallites in polythene during drawing proceeds in two stages and no doubt involves the complete breaking down and re-formation of at least part of the crystalline regions, although there is no significant change in the overall degree of crystallinity on drawing; in the final fully extended state the crystallites are oriented with the molecular chain axes parallel to the direction of drawing.^{15, 16, 17} It is not surprising then that the deformation associated with cold drawing is largely irrecoverable. Some retraction is observed on raising the temperature, due probably to the relaxing of strains in the amorphous regions which

will also be partially oriented, and if the temperature is raised to the crystalline melting point the structure becomes unstable and progressive but regular disordering of the crystallites occurs^{16, 17}. The cold drawing process, combined with appropriate annealing procedure is used in practice to make oriented filaments of polythene with tensile strengths up to 20,000 lb/sq. in.* Reverting to the stress-strain curve in Fig. 9.2, as the specimen is strained further beyond the point *B*, the stress rises again until fracture occurs at some rather ill-defined point, *C*.

The exact shape of the stress-strain curve obtained with any particular polythene depends to some extent on the way in which the tensile specimen is prepared. Specimens made by injection moulding or from extruded material are often "shock-cooled" with the result that the spherulitic structure is not fully formed; such specimens tend to give high elongation at break and low values of yield stress and of ultimate stress. The effect of annealing at elevated temperatures seems to be that the spherulites grow by re-arrangement of the crystallites (there is actually very little change in extent of crystallinity), leading to a "texture" similar to that obtained directly by compression moulding followed by slow cooling. This change is accompanied by an increase in yield stress and, with low molecular weight polythenes, a tendency for fracture to occur during the drawing process in the region *A B*.

An annealing treatment of this kind will also facilitate the relaxation of stresses in the amorphous regions which may affect some mechanical properties in a different way, but the major effect appears to be on the crystalline "texture". Thus annealing influences the behaviour of polythene under both low and high deformations.

Yield stress and yield strain

The dependence of the tensile properties of polythene on temperature, on rate of extension and on the thermal history of the specimens, can be illustrated by the behaviour of the three polythenes *A*, *B* and *C* described in Table 9.3;¹⁸ they cover the molecular weight range of polythenes in general use, and are also typical in having very similar degrees of crystallinity. All the tensile tests were carried out at constant rate of extension.

Table 9.3—CHARACTERISTICS OF POLYTHENES *A*, *B*, & *C*

Property	Designation		
	<i>A</i>	<i>B</i>	<i>C</i>
Density, gm/cc, at 20°C	0.922	0.919 ₆	0.921 ₄
Percentage crystallinity ^a	53	51	52
M.F.I.	0.2	2	20
Molecular weight (\bar{M}_n) ^b	42,000	32,000	22,000

(a) From X-ray diffraction measurements.

(b) Estimated from M.F.I. using Equation 3.

* See Chapter 29.

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on specimens machined from compression moulded sheet which, unless otherwise stated, had received no subsequent annealing treatment. This procedure was adopted to provide specimens in a state corresponding to practical fabrication conditions.

Stress-strain curves for *B* at temperatures between -65° and $+75^{\circ}\text{C}$ are shown in Fig. 9.3; the tests were carried out at a rate of extension of about 200% per minute, calculated on the initial dimensions of the specimens. A very similar family of curves was obtained on testing

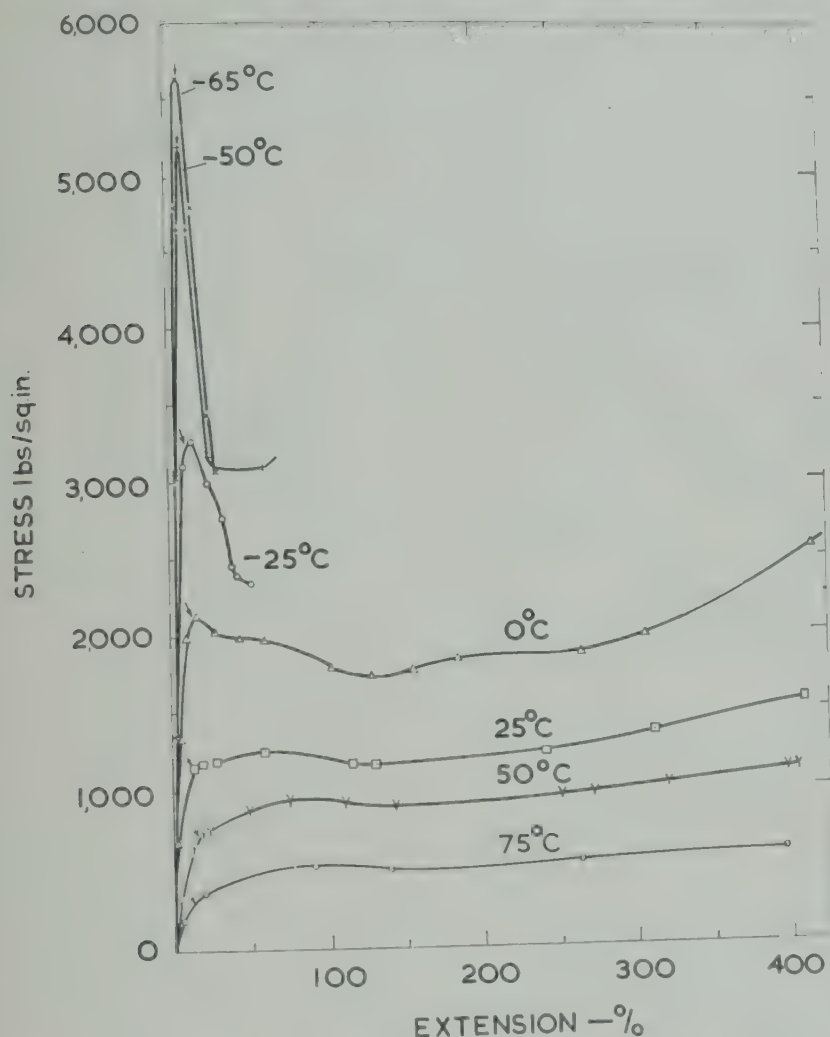


Fig. 9.3. Stress-strain curves for polythene *B* between -65° and $+75^{\circ}\text{C}$: rate of extension 190% per minute

polythene *A*. The lower molecular weight material, *C*, also behaved in much the same way but was rather less ductile, as is shown by the fact that at -50° and -65°C specimens tended to break at extensions below the yield point. From the practical point of view the tensile properties of most importance are the stress and strain at the yield point. As will be apparent from Fig. 9.3, although any definition of these quantities must be somewhat arbitrary it is fairly easy to pick the points on the curves where the slopes start to decrease rapidly; the yield points chosen on

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this basis are indicated on the curves. Fig. 9.4 (a) and (b) show the temperature dependence of yield stress and yield strain for polythenes A, B and C; these data illustrate the point which has already been made, namely that yield stress and strain are not functions of molecular weight. The over-riding dependence on crystallinity, however, is shown by Fig. 9.5 in which yield stress is plotted against density for a range of polythenes. The data are represented by the equation:

$$\text{Yield stress (lb/sq. in.)} = 61,500 (\text{density}) - 55,070 \quad (4)$$

Similar data, but covering an even wider range of polythenes, were reported by Sperati, Franta and Starkweather¹¹, from which Equation 5 was derived. These authors also gave a quantitative relation between density and degree of crystallinity which is discussed in Chapter 7.

$$\text{Yield stress (lb/sq. in.)} = 69,500 (\text{density}) - 62,300 \quad (5)$$

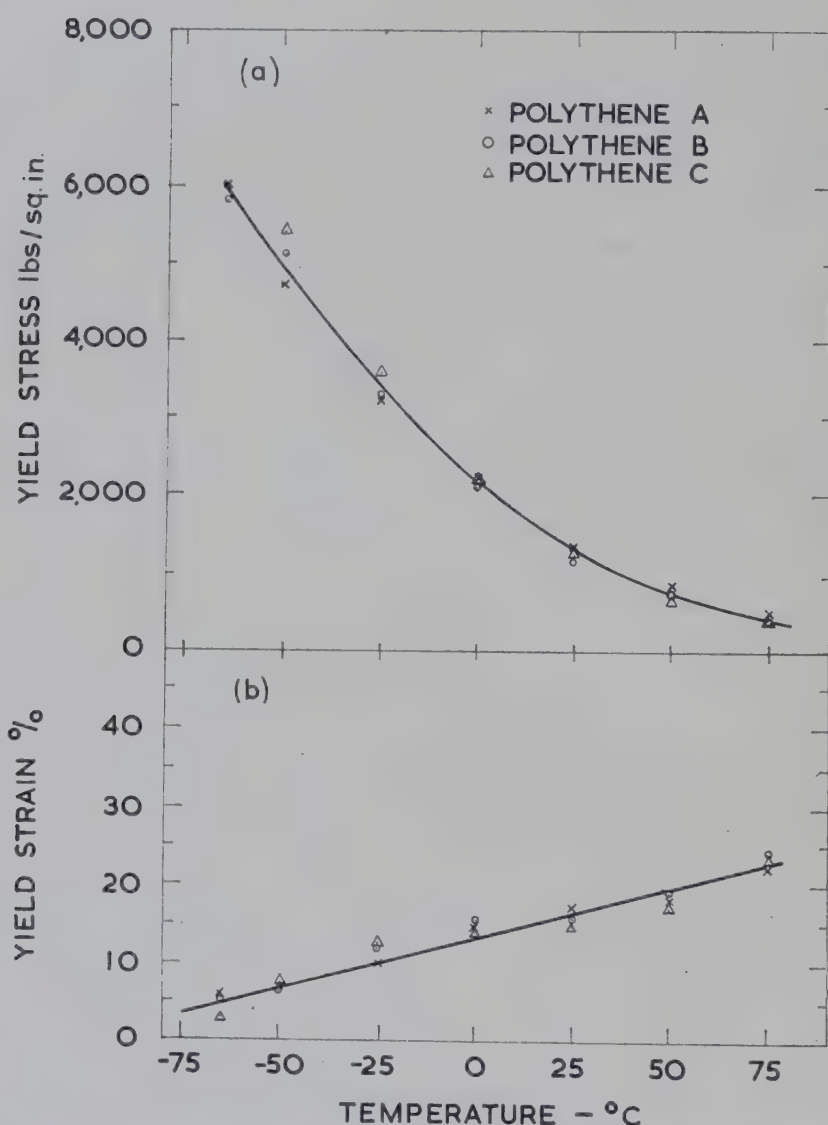


Fig. 9.4. Yield stress and yield strain as functions of temperature for polythenes A, B and C: rate of extension 190% per minute

GENERAL MECHANICAL PROPERTIES

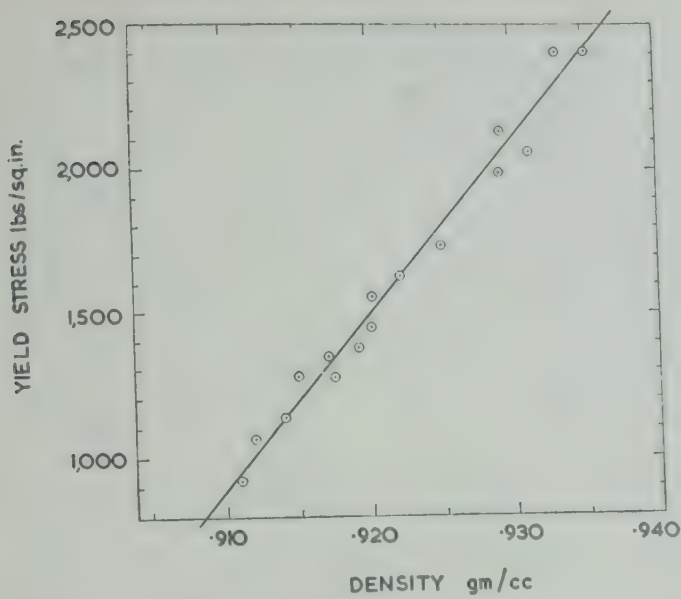


Fig. 9.5. Dependence of yield stress upon density

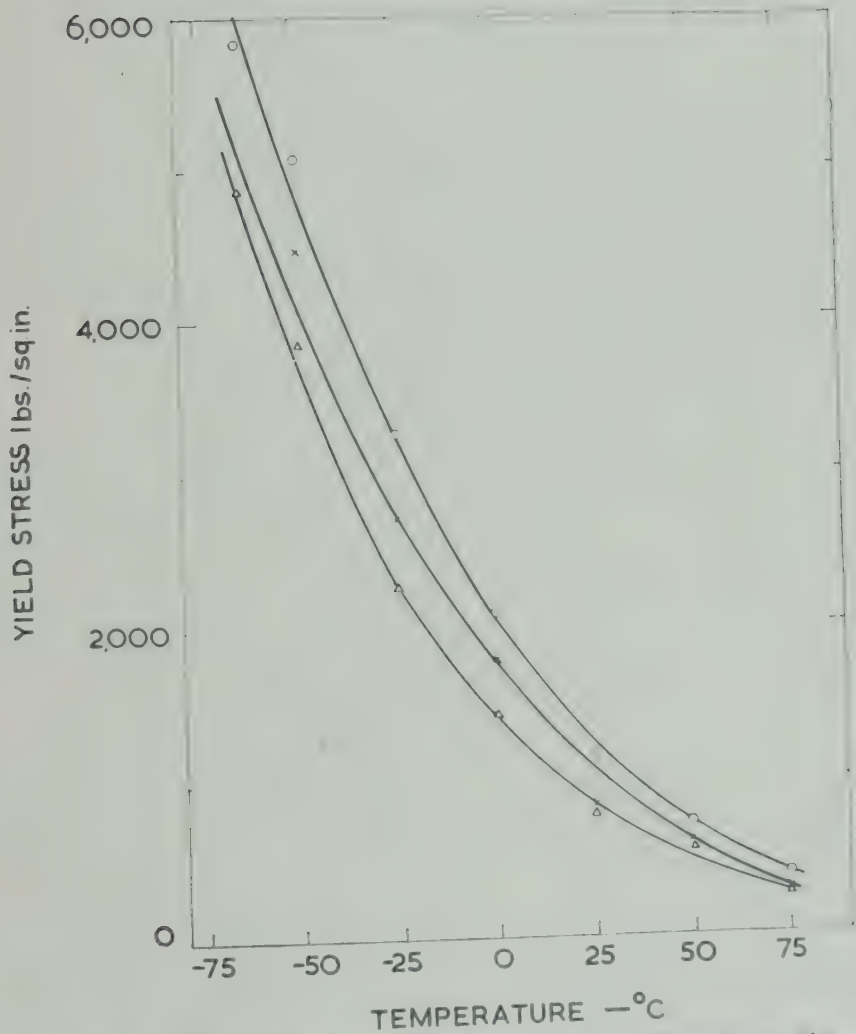


Fig. 9.6. Yield stress v. temperature for polythene B at different rates of extension
○ 190% per minute × 7.7% per minute Δ 0.31% per minute

Precise quantitative agreement on the values of tensile properties between different sets of data is not to be expected. Quite apart from the differences between different polythenes, the results also depend on the exact conditions of test and of the specimens. Thus, the rate at which the specimen is extended is important; Fig. 9.6 shows the temperature dependence of the yield stress of polythene *B* over a range of rates of extension of over 600 : 1. The faster the rate of extension, the higher the yield stress. Permanent changes in properties can be produced by annealing the test specimens. Fig. 9.7 shows the effect of annealing

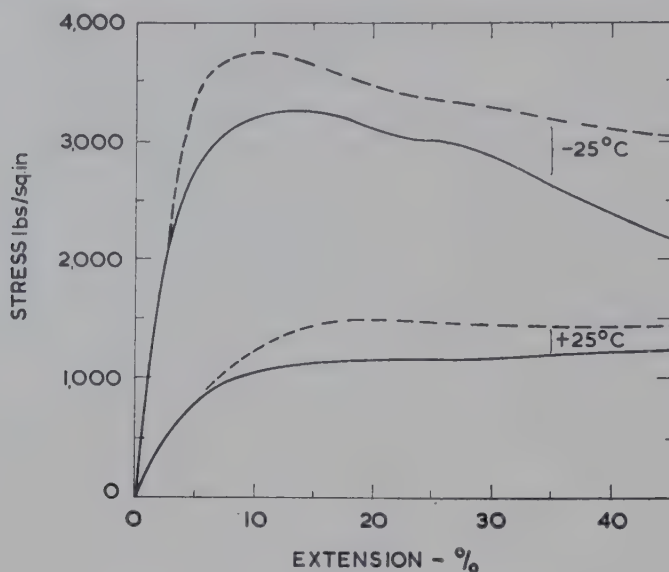


Fig. 9.7. Stress-strain curves for polythene *B* at -25°C and $+25^{\circ}\text{C}$:
rate of extension 190% per minute

— specimens "as moulded"
- - - specimens annealed $\frac{1}{2}$ hr. at 180°C

specimens of polythene *B* for $\frac{1}{2}$ hr. at 180°C ; the specimens were allowed to cool slowly from the annealing temperature. The density increase on annealing was less than 0.002 gm/cc, yet the yield stress at 25°C was raised by about 400 lb/sq. in.

For practical applications an alternative procedure to quoting yield stress and strain has been suggested by Carey, Schulz and Dienes,^{19, 20} in terms of an arbitrarily defined "elastic limit". This involves, however, first determining the modulus at the origin by an extrapolation method; the elastic limit is then defined as that point on the stress-strain curve at which the tangent modulus is one half the modulus at the origin. The whole question of the determination of the modulus at the origin for polythene is discussed below; at this point it may be noted that stresses and strains at the elastic limit computed in this way for polythenes of different molecular weight are quoted by these authors. They find that the extension at the elastic limit is sensibly independent of molecular weight; it is constant at about 1.4% below -40°C , increasing linearly with temperature to about 6.5% at 80°C . The stress at the elastic limit does appear to show some dependence on molecular weight at the higher

temperatures, but converges to a common value below about -40°C . This apparent dependence on molecular weight is unexpected, and may have been the manifestation of a correlation between molecular weight and degree of crystallinity in the polythenes used.

Modulus in tension

Difficulties arise when it comes to quoting modulus figures for polythene. This is apparent from Fig. 9.8 which shows the initial portion of the stress-strain curve up to 1.5% strain for polythene B at 25°C . There is no linear portion, and in fact the curvature increases on approaching the origin; this is true at all higher temperatures and at lower temperatures at least down to -38°C .¹⁸ It is not feasible therefore to determine by graphical means a value for the tangent modulus at the origin, and in any case such a figure would be of no practical value. For practical purposes some convention must be adopted, and one which is currently accepted is to quote an "off-set" or secant modulus at some arbitrary

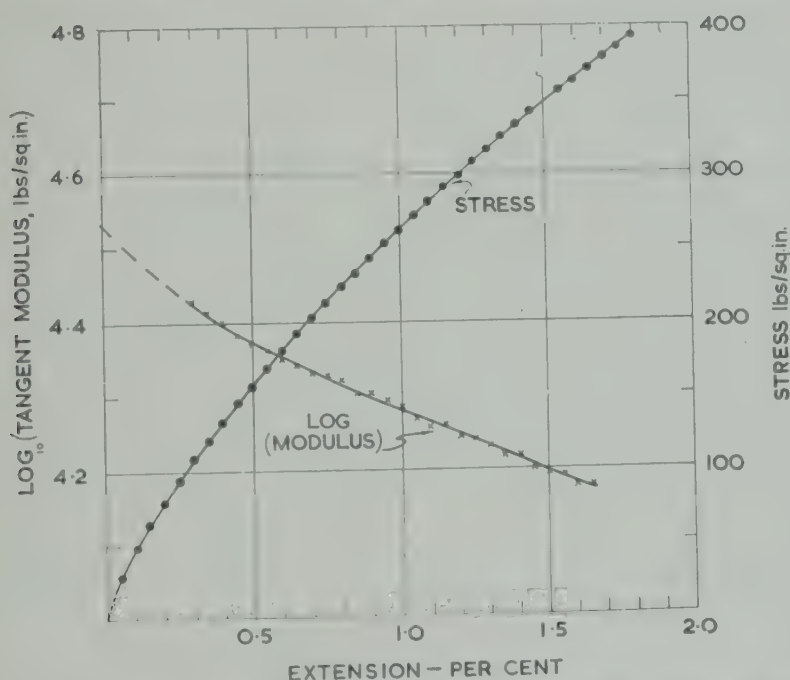


Fig. 9.8. Stress v. strain and log (tangent modulus) v. strain curves for polythene B at 25°C : rate of extension 7.7% per minute

value of strain. Fig. 9.9 shows in fact the "2% secant modulus" for polythenes A, B and C between -65° and $+75^{\circ}\text{C}$, this being the ratio of stress to strain at 2% extension. It will be noted that modulus is sensibly independent of molecular weight; it is in fact largely determined at ordinary temperatures by degree of crystallinity (cf. yield stress and strain).

As would be expected, the 2% secant modulus shows a dependence on rate of extension of the same order as that shown by the yield stress (cf. Fig. 9.6 and 9.10); there is an approximately logarithmic dependence

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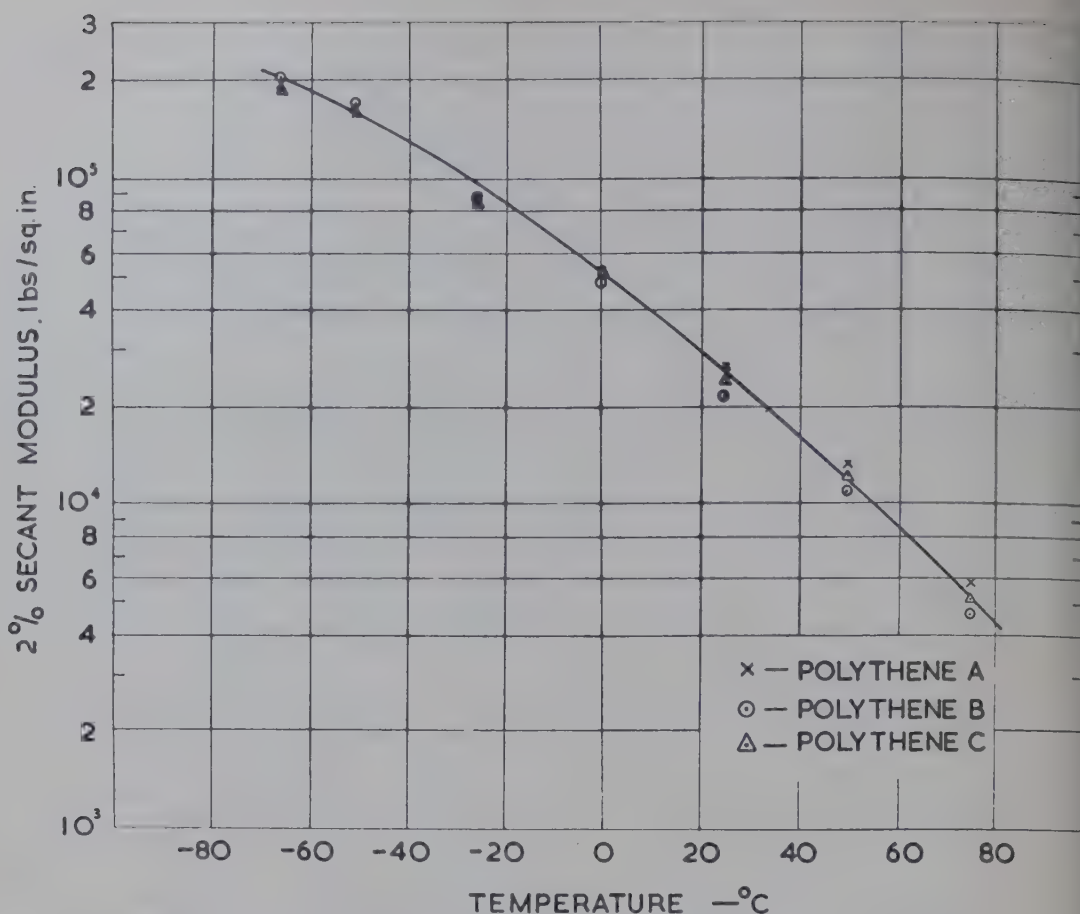


Fig. 9.9. 2% secant modulus v. temperature for polythenes A, B and C: rate of extension 190% per minute

of modulus on extension rate, the modulus increasing by about 20% for every ten-fold increase in extension rate. An effect of this order of magnitude was reported by Carey *et al.*¹⁹ Annealing had little effect on the 2% secant modulus, as may be seen from the stress-strain curves shown in Fig. 9.7.

Tensile modulus at the origin of the stress-strain curve

The difficulty of determining the modulus at the origin has already been referred to above. The extrapolation method suggested by Carey *et al.*^{19, 20} and referred to above, is based on the fact that they found an essentially linear relation between the logarithm of the incremental modulus (i.e. the tangent modulus) and the strain, at strains between about 1% and 10%. Extrapolating to zero strain gave a value for E_0 , the modulus at the origin. These authors obtained values of E_0 on five polythenes of widely different molecular weights by this method from +25° to -30°C; from -30° to -60°C the initial tangent to the stress-strain curve was evaluated graphically, while from -25° to -125°C values of E_0 were computed from shear modulus data obtained in torsion, assuming Poisson's ratio to be 0.5. All these data¹⁹ are shown in Fig. 9.11, and they would suggest that the modulus is a function of molecular weight at high temperatures but not at low temperatures. It

is, however, much more likely that the polythenes had different degrees of crystallinity, increasing regularly with increasing molecular weight. The convergence of the modulus values at low temperatures would then be consistent with a "glass transition" temperature, T_g , of the order of -100°C .

At temperatures approaching T_g , the increasing rigidity of the amorphous regions more and more controls the stiffness of the polymer, whereas at higher temperatures where the amorphous regions are quite rubber-like, it is the degree of crystallinity which largely determines the modulus. The fact that at ordinary temperatures it is the crystallinity which determines the stiffness of polythene is shown by the data plotted in Fig. 9.12.

The values of E_0 were obtained by the logarithmic extrapolation method, and cover a range of nearly 2 : 1. Within this range there is a reasonably linear correlation with density given by Equation 6. There

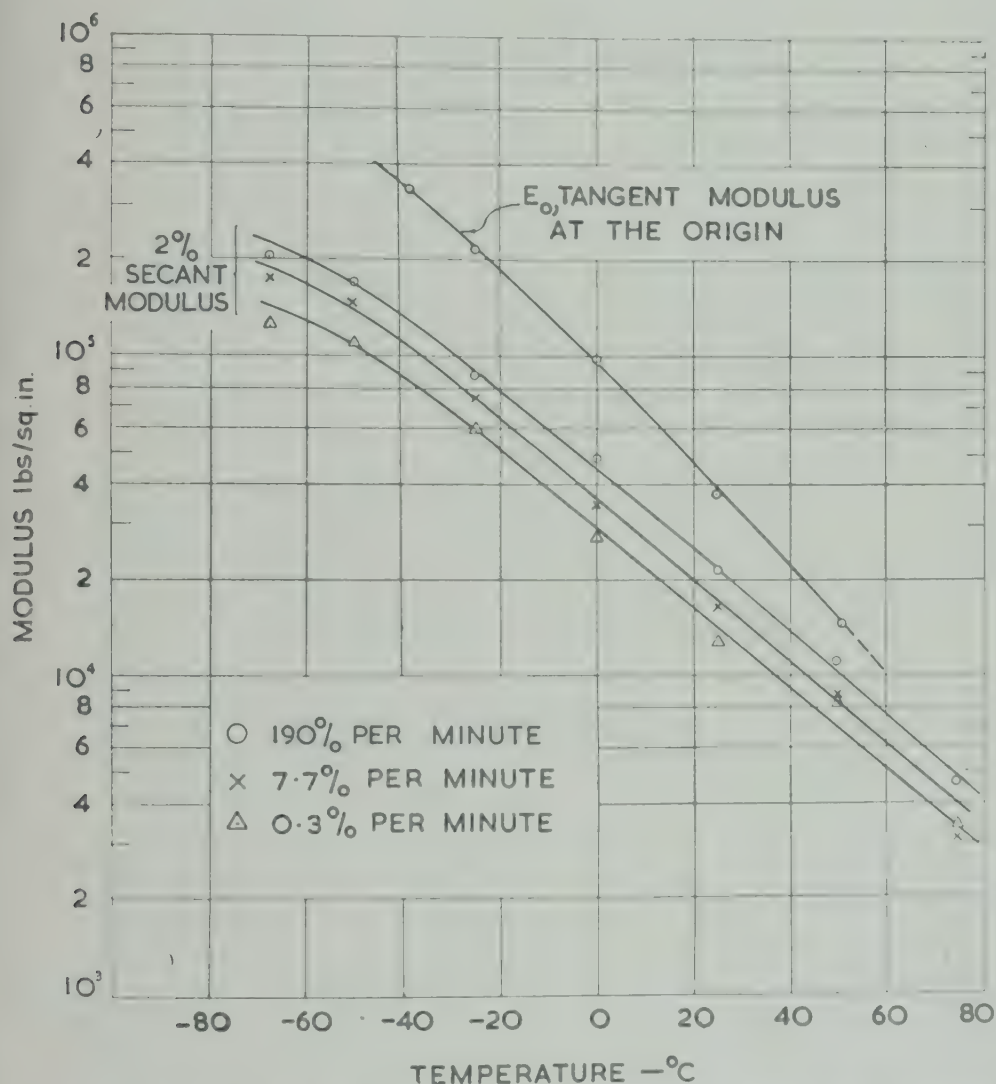


Fig. 9.10. Polythene B: 2% secant modulus v. temperature at three rates of extension: tangent modulus at the origin, E_0 v. temperature

is no correlation with molecular weight (M.F.I.). Over a wider range of densities, 0.90 to 0.94 gm/cc, Sperati *et al.*¹¹ found a logarithmic dependence of stiffness (as determined in flexure) on density given by Equation 7. The data given in Fig. 9.12 are also adequately represented by Equation 7.

$$E_0 \times 10^{-3} = 1900 (\text{density}) - 1723 \quad (6)$$

$$\text{Log (stiffness, lb/sq. in.)} = 26.420 (\text{density}) - 19.889 \quad (7)$$

A more detailed study of the initial portion of the stress-strain curve has recently been made by Sandiford¹⁸ on polythene *B*, at three rates of

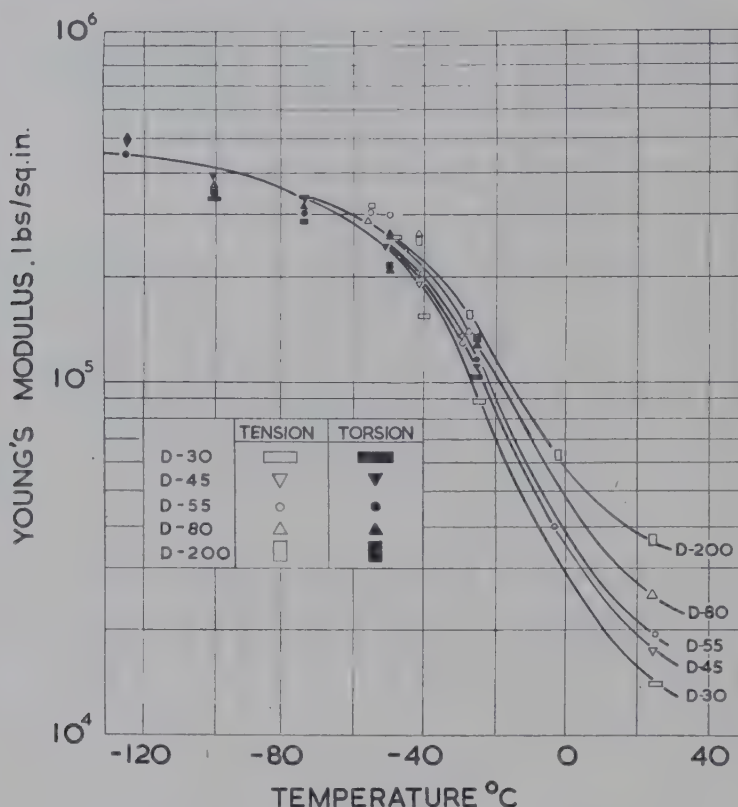


Fig. 9.11. Modulus v. temperature for various polythenes after Carey *et al.*¹⁹

GRADE	RELATIVE MOLECULAR WEIGHT
D-30	16,000
D-45	19,000
D-55	20,000
D-80	26,000
D-200	38,000

straining between -38° and $+50^{\circ}\text{C}$. His measurements extended down to 0.1% strain, and the stress-strain curve in Fig. 9.8 is a typical example of the results obtained. The logarithm of the tangent modulus is also plotted in Fig. 9.8, and it will be noted that the dependence of this quantity on strain is not in fact linear. At strains below 1% the curvature is quite marked reflecting the increasing curvature of the stress-strain curve itself. This departure from linearity was not observed

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by Carey *et al.*,^{19, 20} whose data did not extend below 1% strain. The consequence of this increasing curvature is that even the value of E_0 , the modulus at the origin, obtained by the logarithmic extrapolation technique is rather indeterminate and is probably a minimum estimate.

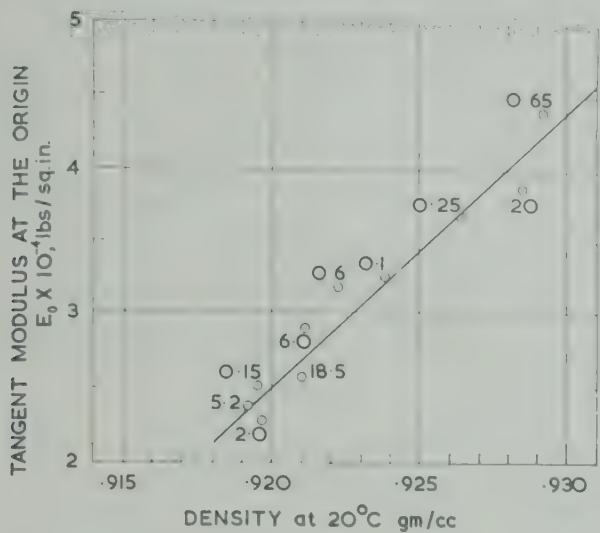


Fig. 9.12. Dependence of E_0 tangent modulus at the origin, on density for various polythenes: M.F.I. values shown for each polythene

However, in the absence of any better approach, values were computed in this way and are shown in Fig. 9.10 for comparison with the 2% secant moduli. These data are further discussed below. The data for polythene B are summarized in Table 9.4.

CREEP BEHAVIOUR

An exact knowledge of the creep characteristics of polythene as a function of time, temperature and stress, in a form that would enable its behaviour to be predicted on the basis of short time tests, would be of great value in the design of such articles as polythene-sheathed cables and pipes for conveying fluids. Some progress has been made in this

Table 9.4—THE DEPENDENCE OF MODULUS ON TEMPERATURE FOR POLYTHENE B: RATE OF EXTENSION 190% PER MIN.

Temperature °C	2% Secant modulus, lb/sq. in.	E_0 , Modulus at the origin, lb/sq. in.
-65	205,000	—
-50	170,000	—
-38	125,000	330,000
-25	88,000	215,000
0	48,000	98,000
25	22,000	38,000
50	11,000	15,000
75	4,500	—

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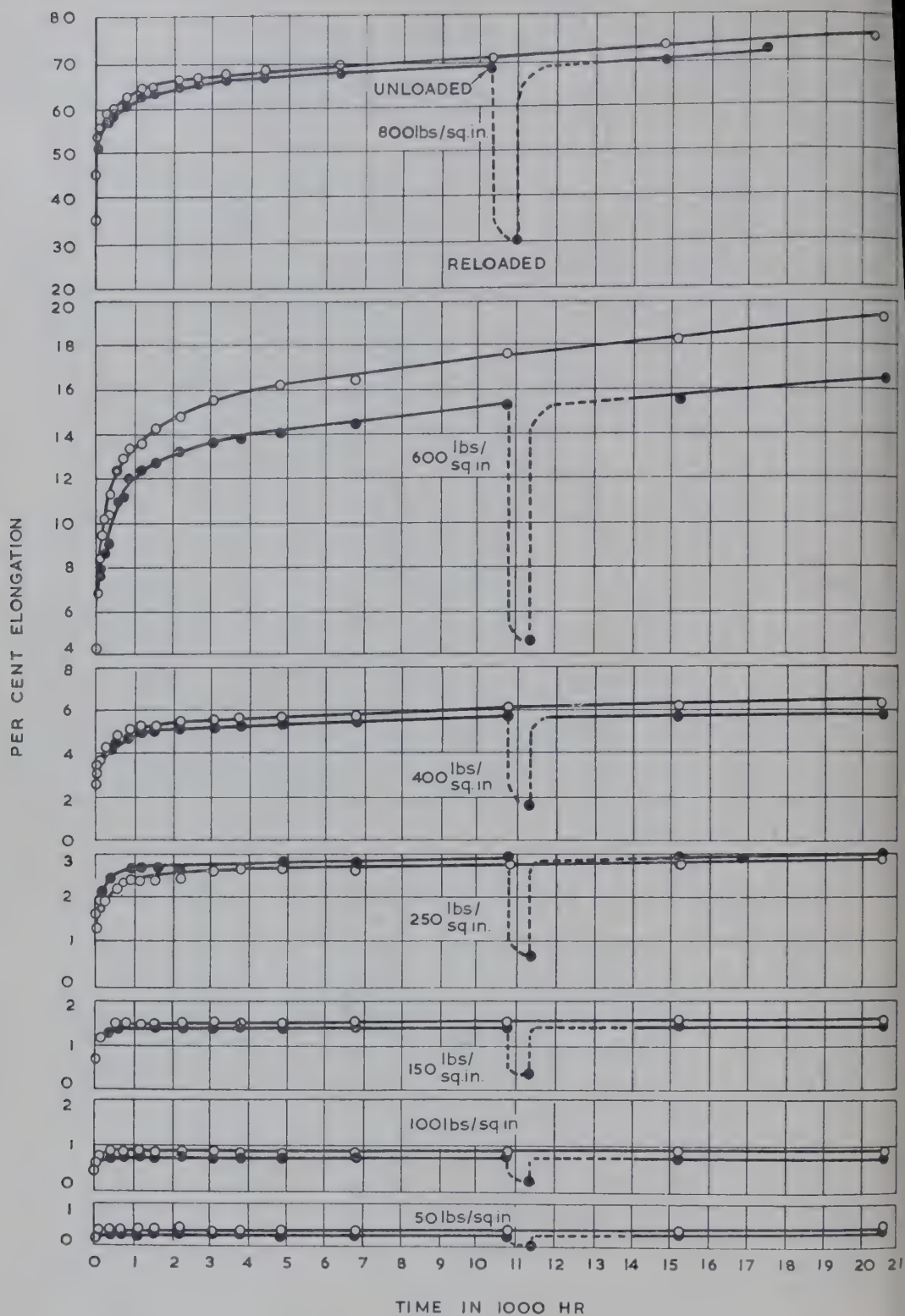


Fig. 9.13. Creep behaviour of polythene at 30°C (85°F) under different stresses

- — ○ Continuous loading: average of two tests
- — ● Interrupted loading: single test

direction, adopting a rather empirical approach, but the data available are not very plentiful.

Creep in tension at constant temperature

The only extensive published work on the creep properties of polythene is due to Gohn, Cummings and Ellis²¹ whose data refer to 30°C (85°F) and cover a time scale of over two years. They investigated four different batches of commercially available polythene, all of very similar molecular weight (M.F.I.s between 1.5 and 2.0²²); three of the batches contained small amounts of carbon black and of anti-oxidant as protection against oxidation. The behaviour of all four materials was very similar, and all may be assumed to have densities similar to that of the "natural" polythene batch, which had a density of 0.917 gm/cc.²² Data obtained on the "natural" polythene at stress levels between 50 and 800 lb/sq. in. are shown in Fig. 9.13; the tests were carried out on compression moulded specimens, of 2 in. gauge length and nominally 0.125 in. thick, in the "as received" condition. The data show that on loading the polythene there is first a rapid and considerable extension, and this stage is complete within a few hours at low stresses but may take many days at

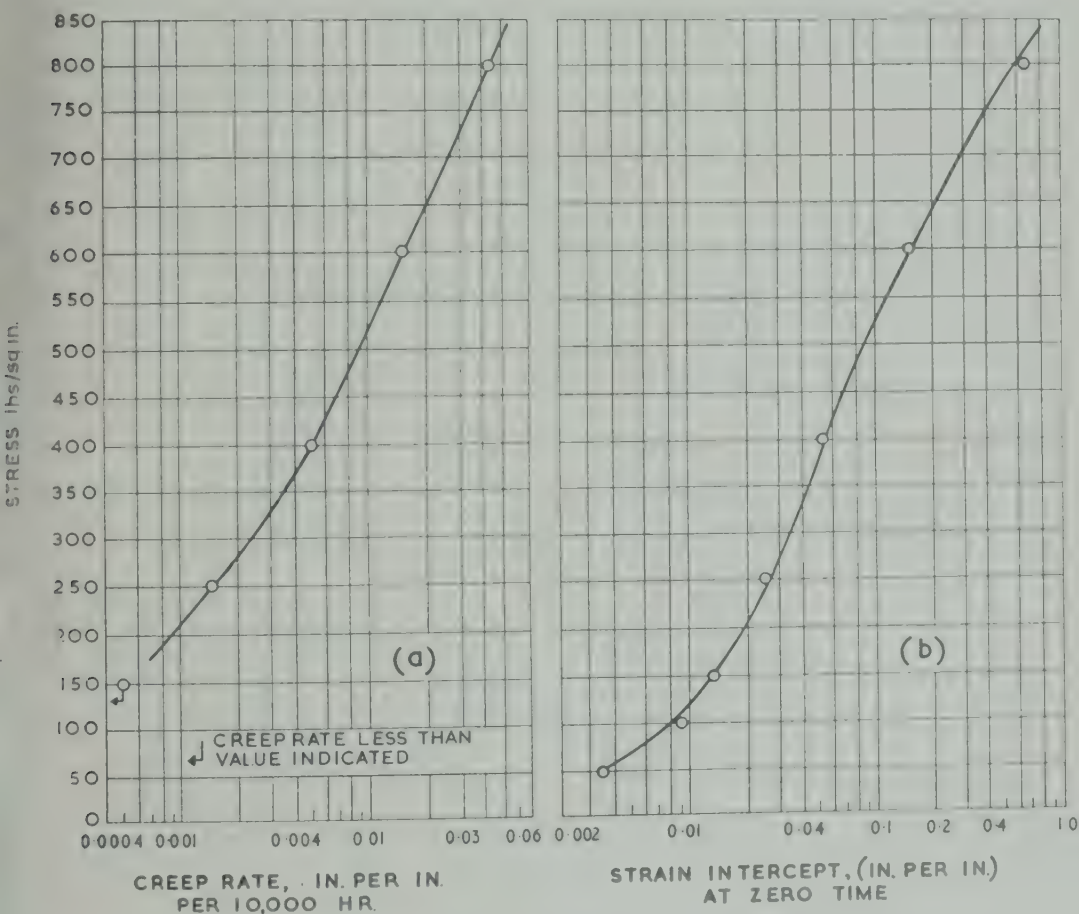


Fig. 9.14. Creep characteristics of polythene at 30°C (85°F) after 10,000 hr.

- (a) Stress v. creep rate
- (b) Stress v. strain intercept at zero time

high stresses. In the second stage the specimen slowly extends at gradually decreasing rate, which does not however appear to attain constant value even after two years (18,000 hrs).

It is tempting to draw an analogy with the behaviour of metals such as lead, which have comparable creep rates at room temperature, but this is not permissible.

Although the creep rate of polythene in the "second stage" is comparable with that of lead alloys at low stresses ($= 400 \text{ lb/sq. in.}$), this creep rate is attained only after a much more rapid and substantial initial elongation. Furthermore, polythene specimens show rapid and considerable elastic recovery on removal of the load, even at quite high stresses; the extent of recovery increases in an exponential manner with time and goes virtually to completion if the initial strain does not exceed about 5%.²³ The data shown in Fig. 9.13 illustrate the fact that unloading and re-loading the specimens has little effect on their subsequent be-

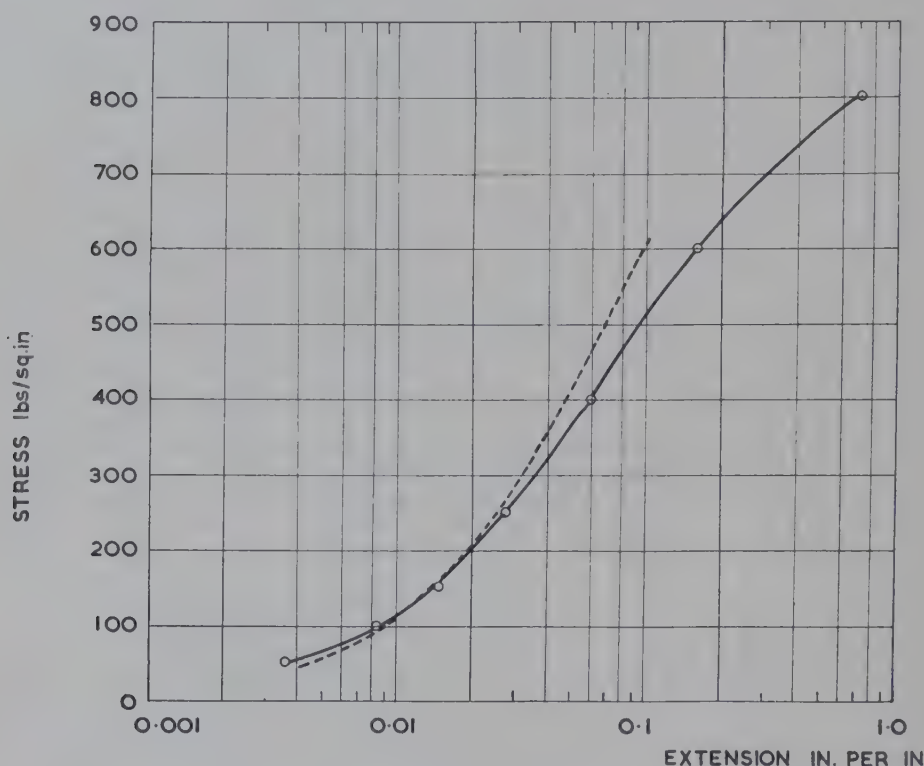


Fig. 9.15. Total creep of polythene at 30°C (85°F) after 10,000 hr.

—○— Experimental data of Gohn et al.²¹
 - - - - Equation (9), adjusted to 30°C

haviour. Creep in polythene is in fact essentially a time-dependent elastic phenomenon; the term "visco-elasticity" is used to cover such behaviour which is associated with substances having very long molecules. Creep in metals, however, is essentially due to plastic flow (ignoring the minor contribution due to instantaneous elastic deformation), and this is irrecoverable. It proceeds at a more or less constant rate, which means

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that under dead-weight loading conditions a "tertiary stage" of creep sets in after some time, leading rapidly to fracture.

Gohn *et al.* have summarized the long-term creep characteristics of polythene by presenting the position after 10,000 hrs (14 months). This is shown in Fig. 9.14 and 9.15. Fig. 9.14 (a) gives the creep rate as a

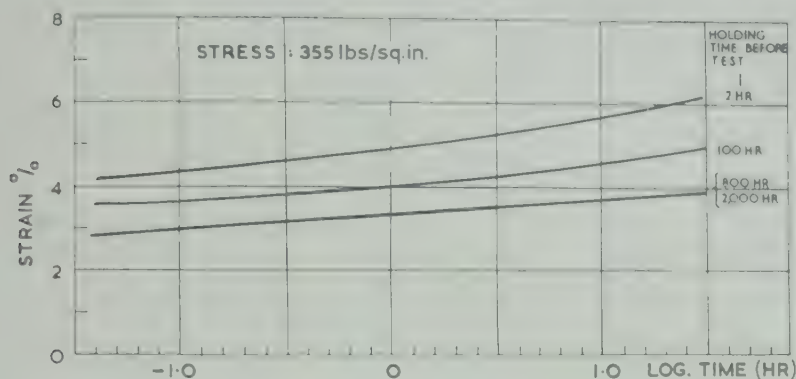


Fig. 9.16. Creep of polythene at 40°C: the effect of holding at 40°C before test

function of stress after this time, and Fig. 9.14 (b) gives the corresponding strain intercepts at zero time for these creep rates, which are a guide to the initial short-time extensions. Fig. 9.15 is a "10,000 hour" stress-strain curve, plotted with a logarithmic strain scale to facilitate interpolation.

The effect of temperature

The creep behaviour of polythene between 20°C and 80°C has been investigated by Hoff and Sherrard Smith²⁴ over the relatively short time of about twelve days; most of the work done was in the range of creep strains below 10% extension. Commercial quality polythene (M.F.I. = 2) was used in the form of $\frac{1}{8}$ in. diameter monofilament extruded under conditions chosen to produce the monofilament as strain-free as possible; the tests were carried out on specimens in the "as received" condition, in which they had a density of 0.918 gm/cc.

Some preliminary work was, however, carried out to investigate the effect of thermal treatment, with rather unexpected results. Fig. 9.16 shows creep curves at a 355 lb/sq. in. stress level at 40°C, plotted on a logarithmic time scale, for specimens which had been held for times up to 2,000 hrs at 40°C before testing. It can be seen that both the creep strain and the creep rate are reduced by this very mild annealing treatment, which is substantially complete in 800 hrs. The same effects were produced by annealing for shorter times at higher temperatures, e.g. 50° and 60°C, provided that the specimens were subsequently cooled *very slowly* to the test temperature of 40°C. It is probable that the same process was responsible for the "shelf-ageing" effect observed by Gohn *et al.*²¹ who found a similar effect on creep behaviour at 30°C on storing samples for periods of 1 to 2 years at 30°C. The mechanism of this process is obscure, but it is probable that it involves the equilibration of

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the spherulitic structure of the polythene rather than any change in the actual extent of crystallinity or a gross re-ordering of the amorphous phase: it is not accompanied by any significant change either in specimen dimensions or density.²⁴

Curves of extension as a function of time for polythene at 20° and 40° under dead-weight loading at nominal stress levels between 265 and 890 lb/sq. in. are shown in Fig. 9.17 and 9.18.²⁴ A logarithmic time scale

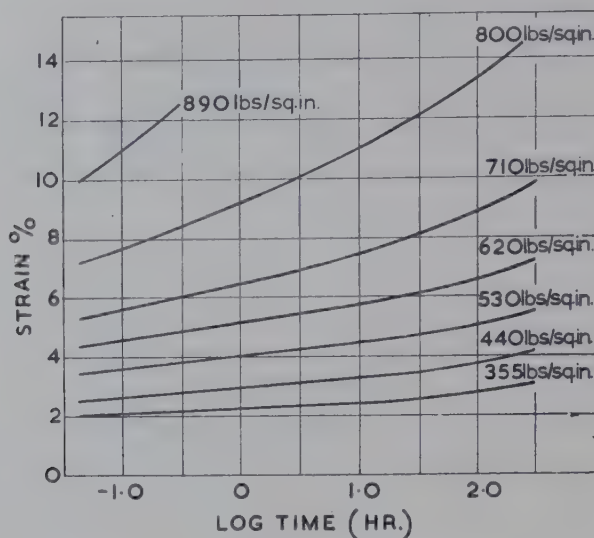


Fig. 9.17. Creep of polythene at 20°C

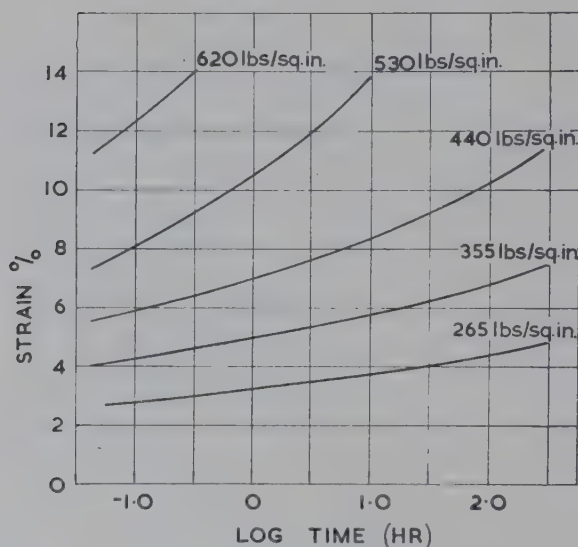


Fig. 9.18. Creep of polythene at 40°C

has been chosen for convenience of presentation since the exact form of the initial part of the curve is of little importance. The effect of temperature is brought out in Fig. 9.19 which shows the creep strain after 280 hours as a function of temperature at three different stress levels. It is apparent that the dependence of creep strain on temperature is approximately linear from 20° to about 40° or 50°C, but that at higher temperatures the creep strain increases very rapidly especially at the higher

stresses. This is almost certainly due to the melting of the crystalline regions, which sets in at temperatures around 50°C and which affects other mechanical properties in a similar way (cf. sections above "General considerations" and "Properties in tension"). In effect the nature of the material is progressively changing above this temperature.

As a corollary to this view, it would be expected that, at ordinary temperatures and for small strains, the order of magnitude of extension in creep but not its time-dependence would be determined largely by the degree of crystallinity, as are the yield stress and modulus (Fig. 9.5 and 9.12). Direct evidence is lacking, but Oakes²³ found that at strains

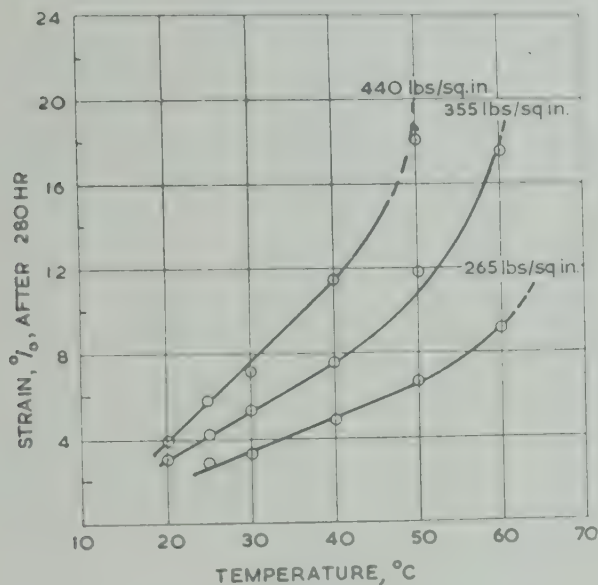


Fig. 9.19. The dependence of creep strain after 280 hr. on temperature and stress

below 10% over short times creep behaviour showed no significant dependence on molecular weight for polythenes of approximately the same densities.

Creep at constant stress: prediction of long time creep

The data so far quoted were obtained in fact on specimens subjected to a gradually increasing stress arising from the progressive diminution in cross-section with increasing extension. Hoff and Sherrard Smith²⁴ have calculated creep curves at constant stress from their experimental data, and a typical family of curves for creep at 355 lb/sq. in., at different temperatures is shown in Fig. 9.20.

For certain polymers the effects of time and temperature on their response to applied stresses may be considered equivalent. Assuming this to be so, Ferry^{25, 26} has shown that stress-response data obtained in short times over a wide temperature range can be used to predict behaviour over long times at a given low temperature. This "reduction principle" was in effect applied independently by Conant, Hall and Lyons²⁷ to

creep and recovery data obtained on synthetic rubbers.* Its application to the data shown in Fig. 9.20 leads to the 355 lb/sq. in., stress-level curve of Fig. 9.21; the procedure is simply to shift the high temperature creep curves in Fig. 9.20 to the right along the log (time) axis until they mate together to give one smooth continuous "master curve", using the 20°C curve as the datum line. The amount by which any curve is moved,

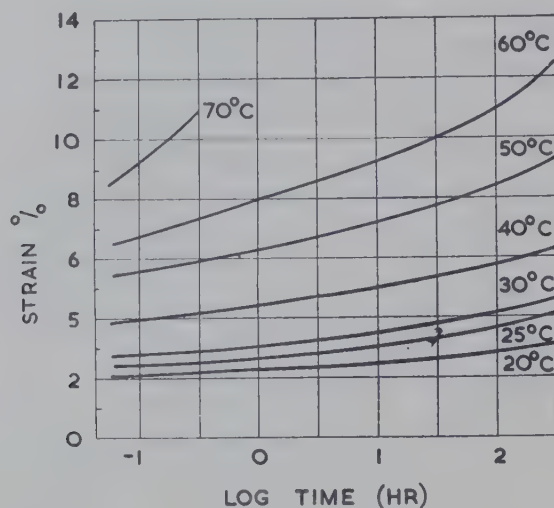


Fig. 9.20. Creep of polythene at constant stress: 355 lb/sq.in., temperatures from 20° to 70°C

in units of log (time), is the "shift factor" F ; the master curves up to 10% creep strain for other stress levels up to 530 lb/sq. in., which represents the upper limit of stresses of practical interest, were obtained in the same way and are shown in Fig. 9.21: The shift factors appropriate to each temperature are given in Table 9.5. In the construction of the master curves actually shown in Fig. 9.21 only the data obtained at 40°C and at lower temperatures were used, since it has been shown

Table 9.5

Temperature °C	Shift factor, F Units of log (time hrs)
20	0
25	2.0
30	3.0
40	5.6
50	7.4
60	9.1
70	11.0
80	12.3

* The "reduction principle" is normally considered to be applicable only to certain amorphous polymers, since for crystalline ones changes in degree of crystallinity and crystallite organization due to temperature changes affect stress-response characteristics in an unpredictable way. However, the proof of the pudding is in the eating, and the application of the principle to polythene over a carefully chosen narrow temperature range does appear to be justified.

Fig. 9.19) that at 50°C there is a sharp change in creep behaviour. This is also shown by the change in the apparent activation energy of creep E_c . Treating creep as a rate process,²⁵ and interpreting F as the logarithm of a reciprocal creep rate, E_c is given by Equation 8. Applying this equation to the data given in Table 9.5, E_c is found to have a value of 18 k.cal/mole below 50°C, falling to about 83 k.cal/mole at higher temperatures.

$$F = \text{constant} + E_c/2.3 RT \quad (8)$$

It was found empirically²⁴ that the master curves in Fig. 9.21 are described with fair accuracy by Equation 9 where the stress is expressed in lb/sq. in., strain in percent extension and time in hours:

$$\log (\text{stress}) = \log (\text{strain}) - 0.0283 (\text{strain}) - 0.0409 \log (\text{time}) + 2.238 \quad (9)$$

This equation only holds for creep strains up to 10%. The master curves, and this equation, may be applied to temperatures other than 20°C (but

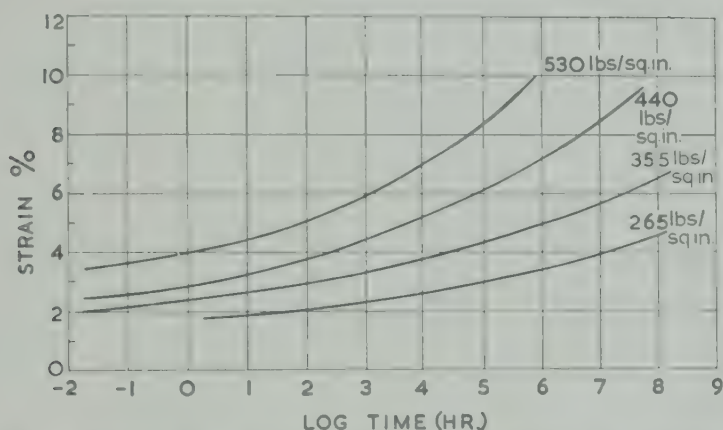


Fig. 9.21. Creep of polythene at constant stress: "master curves" for different stresses at 20°C

not higher than 40°C) by use of the appropriate shift factors given in Table 9.5. If the equation is used, the shift factor is simply subtracted from the numerical value of $\log (\text{time})$; if the master curves are to be used, they must be displaced to the left along the $\log (\text{time})$ axis by the value of the shift factor. It is to permit this use of the master curves that they are shown in full in Fig. 9.21, covering a time scale of several thousand years. In practice extrapolation to a few years is all that could reasonably be attempted; in fact, adjusting the 355 lb/sq. in. curve to 40°C permits extrapolation to just less than one year.

When master curves of this type are used for the prediction of long-time creep behaviour under constant load, it must be remembered that they apply to creep under constant stress; a correction must therefore be made to the creep strain to take into account the increase in stress which occurs on extension. At low stresses equivalent to strains less than 10%, which is the region to which this procedure is probably restricted, the correction will be small and will be of the same order as the percentage

strain. This technique for predicting long-time creep behaviour from data obtained over short times at different temperatures has not yet been verified experimentally over long periods of time. An indication of the utility of this approach is provided by a comparison of the experimental data given by Gohn *et al.*²¹ for creep strain as a function of stress at 10,000 hrs (14 months) at 30°C with the values predicted by Equation (1) on the basis of experiments for times not exceeding 280 hrs. The "10,000 hrs" stress-strain curves are shown in Fig. 9.15; up to stresses of 450 lb/sq. in. the agreement is quite reasonable, and would be slightly improved by correcting the theoretical curve to "dead-weight" loading. Better agreement could hardly be expected between data obtained on different polythenes, although they do in fact have quite similar molecular weights and degrees of crystallinity as judged by M.F.I. and density values (see above).

Creep in compression

There has been no extensive work published on the long term behaviour of polythene under compressive stresses. Work by Oakes²³ has established that for deformations up to a few percent the behaviour of polythene in compression is qualitatively and quantitatively very similar to that in tension. The deformation is roughly proportional to the logarithm of the time, and recovery on unloading is virtually complete, and shows a similar dependence on time. This behaviour is maintained in compression at temperatures up to 90°C. It appears also that for long times and high stresses creep in compression is less than in tension; no doubt this is in part due to the fact that in tension the actual stress is increasing as the specimen extends. However the same conclusion may be deduced in a qualitative way from the results of various empirical tests, on fabricated components such as cables, carried out at elevated temperatures for periods up to two years.²⁸

BEHAVIOUR UNDER COMPLEX STRESSES AND IN THE PRESENCE OF LIQUIDS

Under simple tensile stresses polythene behaves as a tough, ductile material and elongates several hundred percent before breaking; it will also withstand quite high tensile stresses for long periods without fracture, although elongating considerably in the process (cf. Fig. 9.13). However, under conditions of multi-axial stressing it is found that ductility becomes strongly dependent on molecular weight; brittle fracture at quite low elongations can occur, and this effect is drastically accentuated by the presence of certain liquids. The mechanism of all these effects is rather obscure, but they are of great importance in practical applications.

Complex stressing of polythene

Hopkins, Baker and Howard²⁹ have investigated the stress-strain behaviour of polythene under biaxial tensile stresses. Most of their work was carried out on specimens in the form of discs; these were stressed by blowing them up into bubbles. From photographic recording of the changes in dimensions, and a knowledge of the corresponding

pressures, stress-strain curves were computed. For specimens stressed in this way the principal stresses are in the ratio 1 : 1, and it was noted experimentally that the strains in both directions were identical. Of two polythenes *A* and *C* investigated, having molecular weights in the region of 25–30,000,* *C* fractured at strains of less than 20% in a brittle manner without cold drawing, while *A* consistently elongated of the order of 200% with cold drawing. Both materials showed cold drawing, and behaved comparably, in uniaxial tensile tests. Investigation of a series of polythenes indicated a rough correlation with molecular weight: brittle fracture associated with low elongation tends to occur below about 27,000,* while cold drawing and high elongation are the rule above this value. A similar correlation was observed by Hoff,³¹ who also found that the critical molecular weight was in the region of 27,000, corresponding to a polythene with an M.F.I. of about 7. This author also found that ductility in biaxial stressing was considerably enhanced by incorporating as little as 5% of polyisobutylene. Factors other than just molecular weight are probably also involved, including molecular weight distribution, degree of crystallinity and the precise structure of the crystalline regions. For instance, removal by solvent extraction of less than 10% of low molecular weight material from a sample showing brittle behaviour converted it into a ductile material, although the change in average molecular weight was quite small; also the form of the biaxial stress-strain curves could be slightly affected by quenching the samples; the effect of large changes in the degree of crystallinity from one polythene to another was not investigated.²⁹ Hopkins *et al.* also carried out some experiments on thin walled polythene tubes, for which the principal stresses have a 2 : 1 ratio; the results were quite comparable with those obtained on the disc specimens.

The reasons for these complicated effects are obscure. It is quite reasonable that polythene should be less ductile and give brittle fractures in biaxial tension but not in uniaxial tension. This is a manifestation of a general phenomenon: brittle fracture becomes progressively more probable passing from uniaxial to biaxial tension, and is inevitable in triaxial tension. The interesting feature in this case is the rather critical dependence of the transition to brittle fracture on molecular weight; and the other observations quoted indicate that this transition is also a function of the interaction between the amorphous and crystalline regions, perhaps due to differences in the way in which crystallites can accommodate themselves to biaxial deformations. There appears to be some link between these effects and the behaviour of polythene in the presence of polar liquids, which is described below.

The effect of solvents

Although polythene is insoluble in all solvents below about 60°C, solvents for polythene are absorbed at room temperature and swell it, the swelling being greater for material having the lower molecular

* Estimated from relative viscosities quoted by Hopkins *et al.* using solution viscosity data given by Harris.³⁰

weights. The process is slow and reversible, and it may take several days for equilibrium conditions to be attained. In general the effect of the swelling agents depends on the amount absorbed, and a few percent, e.g. xylene or mineral oil, has little effect on the toughness and flexibility of high molecular weight polythene;^{28, 32} swollen polythene has, however, a greater tendency to show brittle fracture under biaxial stress, due presumably to a general weakening of cohesive forces.²⁹ Low molecular weight materials become rather "cheesy" when heavily swollen and can no longer be cold drawn.

The effect of polar liquids: "environmental cracking"

Certain polar liquids, which are in general not solvents for polythene, have an instantaneous and quite profound effect on the fracture characteristics of some polythenes which is apparently exerted through a surface action. Thus exposure of low molecular weight polythene to such substances as acetone, the lower alcohols or nitrobenzene, either as liquid or vapour, causes intense embrittlement on flexure.³² This phenomenon, which has been termed "environmental cracking", is exhibited only when an external multiaxial stress is applied at the same time as an "active agent". High molecular weight polythene is immune.

This phenomenon of environmental cracking came into prominence as a result of the failure in service of polythene sheathed cables in underground ducts which were contaminated with a variety of greases and lubricants, and has since been extensively investigated.³³ Carey³⁴ found that the effect was not shown up in simple tensile tests even in the lower molecular weight materials if injection moulded specimens, which

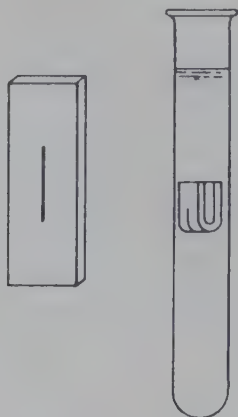


Fig. 9.22. Environmental cracking: test specimen and test assembly

had perfectly smooth surfaces and edges, were used. However, specimens die cut from sheet definitely broke at lower strains when tested in ethyl alcohol than when tested in air. This was interpreted as being due to minor surface imperfections acting as "stress-raisers" and points where multi-axial stresses were developed. For comparative purposes, more reproducible results were obtained by drilling small holes through the centres of the injection moulded tensile specimens. Hopkins *et al.*²⁹ had previously noted that embrittlement by alcohols, esters, etc., occurred

GENERAL MECHANICAL PROPERTIES

much faster under biaxial tension than under uniaxial tension, and that high molecular weight polythene was resistant to this effect.

A simple although rather qualitative method suitable for long time tests was devised by DeCoste, Malm and Wallder³⁵ and is now widely used. On one face of a specimen 0.5 in. \times 1.5 in \times 0.125 in. a slit is cut with a razor blade 0.75 in. long and 0.020 in. deep along the centre line; the specimen is then bent with the scored side in tension and immersed in the liquid under test in an 18 mm dia. test tube (see Fig. 9.22). The test is carried out at 50°C and the time noted at which cracks first appear; these usually begin at the base of the slit, a region of high and complex stress, and propagate at right angles to it. By this test liquids were classified in terms of their cracking activity (see Table 9.6), and polythenes were tested for their resistance to cracking. For the latter purpose a highly active agent was chosen, namely Igepal CA, an alkyl aryl polyethylene glycol ether. Tests with Igepal CA using this bent strip technique showed that polythene of M.F.I. less than 0.4 is practically completely resistant to cracking.* The reliability of this test method has been shown in practice by the satisfactory performance of cable sheaths fabricated from high molecular weight polythene.³³

When a cable is bent the polythene is constrained in one position and stress relaxation undoubtedly occurs; this will also happen in the bent strip test. In neither case are the stresses well defined. These disadvantages were overcome by Ellis and Cummings³⁷ who carried out tests at constant stress for periods up to 14 months on thin walled tubes made from three polythene batches of different molecular weights. The geometry of the test specimen ensured a biaxial stress ratio of 2 : 1, this being the ratio of circumferential to longitudinal stress. The tubes were coated externally with Igepal CA, and held at circumferential stresses between 400 and 1,400 lb/sq. in. No tubes made from the polythene of highest molecular weight (M.F.I. \sim 0.3)* had failed after 14 months at stresses below 1,100 lb/sq. in. The tubes made from the batches of lower molecular weight failed at lower stresses and shorter times. This work provides

Table 9.6—CLASSIFICATION OF MATERIALS AS CRACKING AGENTS FOR POLYTHENE

Active	Inactive
Alcohols Liquid hydrocarbons Organic esters Metallic soaps Sulphated and sulphonated alcohols Polyglycol ethers Silicone fluids	Water Polyhydric alcohols Sugars Hydrolyzed protein Rosin Selected asphalts Selected saponins Acid and neutral inorganic salts

* The molecular weights of the polythenes used were characterized in terms of Williams Plasticity Numbers, which have however been correlated with M.F.I. or "Viscosity Grade".³⁶

quantitative evidence of immunity towards environmental cracking of polythene of M.F.I. less than about 0.5.

Protection from environmental cracking is also imparted to polythene by comparatively small amounts of polyisobutylene; thus 5 to 10% of this polymer compounded with polythene of M.F.I. = 2 gives a material which is quite immune to cracking.³⁵ It is also found that polythene in the form of moulded, unoriented samples is made more resistant to environmental cracking by "quenching", i.e. by rapid cooling from fabricating temperatures. This effect is however only temporary and the polythene reverts to its normal behaviour on storage at room temperature for some days, or more rapidly on annealing at elevated temperatures. Molecular orientation, especially surface orientation, enhances the susceptibility of polythene to environmental cracking; this means that if specimens are prepared by extrusion, quenching has a bad effect since it produces a strained and oriented surface.

There is no generally accepted explanation for this phenomenon of environmental cracking, but it does seem to be significant that it is associated with multi-axial stressing. Even in the absence of "active agents" the behaviour of polythene under biaxial stresses is dependent apparently on molecular weight. As suggested above, the primary correlation in both cases may be with the crystalline/amorphous "texture" of the polythene; Richards² has put forward a tentative explanation on these lines, suggesting that it is the cohesion between crystalline regions which is both a function of molecular chain length and also affected at the surface by the environment.

LOW TEMPERATURE FLEXIBILITY

The fact that polythene retains its flexibility down to very low temperatures has been turned to good account in the design of a wide variety of cables, pipes and other articles which must withstand severe climatic variations in service. A number of tests have been devised for measuring the temperature at which polythene and other plastics and rubbers become brittle. In most of them a simple rectangular specimen of standard size is bent rapidly to a defined extent; the test is carried out on a number of specimens at different temperatures, and that temperature is noted above which none, or some definite percentage, of the specimens break. This is quoted as the "brittleness temperature", suitably defined.

Tests carried out in this way have shown that the brittleness temperature of polythene is dependent on its molecular weight, and also that the scatter of test results is rather large. Thus Hunter and Oakes³⁸ found that the polythene of M.F.I. = 20, available in 1945, had an average brittleness temperature (temperature at which 50% of the specimens failed) of about -25°C , whereas materials of high molecular weight (M.F.I. < 0.7) were still flexible at -100°C . Richards² later reported that polythenes of molecular weights greater than 40,000 had brittleness temperatures in the region of -140°C , which appears to be the lower limiting value for polythene. This author also noted that in the inter-

mediate ranges of molecular weight the values obtained were dependent on the degree of crystallinity of the polymer and on the state of its crystalline "texture". Thus the lower the degree of crystallinity, the lower the brittleness temperature; and the brittleness temperature of a polythene can be lowered by shock-cooling the specimens, although this effect is only temporary and can be readily annulled by an annealing treatment.

Another method of improving the low temperature flexibility of the lower molecular weight polythenes is to incorporate a small percentage of polyisobutylene, e.g. the addition of $12\frac{1}{2}\%$ to a particular polythene lowered its brittleness temperature from -25°C to -45°C .³⁸ This beneficial effect is not however conferred on materials of higher molecular weight which by themselves have good flexibility at low temperatures. It has been found that the measurement of changes in low temperature flexibility provides a convenient way of following the deterioration of polythene on outdoor exposure, and of assessing the value of remedial measures. The deterioration is caused by photo-catalyzed oxidation, and this can be almost completely inhibited* by dispersing in the polythene finely divided carbon black.^{33,39} The test method extensively used in these investigations is that standardized by the American Society for Testing Materials—A.S.T.M. Method D 746-54.T⁴⁰. The development of the apparatus, and a description of its use, has been given by Smith and Dienes.⁴¹ In this method the brittleness temperature, T_b , is defined as that temperature at which 50% of the specimens break; the actual temperature range between complete failure and no failures may be as much as 40°C . The values of T_b obtained by this method tend to be rather lower,³⁹ for comparable materials, than those quoted by Hunter and Oakes³⁸ and by Richards.²

It is difficult to give an unambiguous interpretation of all these results. However it does appear reasonable to associate the lower limiting value of T_b in the region of -140°C with the "glass transition" temperature or so-called "second order transition",¹⁰ in the amorphous regions; this is consistent with the convergence of the modulus values of different polythenes at low temperatures referred to above, and with the dynamic mechanical properties which are discussed later. If this interpretation is correct, then there must be some mechanism peculiar to polythene which is responsible for the higher values of T_b obtained with low molecular weight materials, and for the modifying effects of crystallinity, quenching and additives on them.

It is significant, perhaps, that there is a parallel between these phenomena and the phenomena associated with the environmental cracking produced by polar liquids: the effects of molecular weight, quenching and the presence of small amounts of polyisobutylene, are all analogous.² Since environmental cracking seems to be associated with the surface condition of the specimens, and to be promoted by "stress-raisers" or

* Cf. Chapter 6.

"notches" where complex stresses are developed, it is at least highly probable that similar effects operate to raise the brittleness temperature of low molecular weight polythenes above the expected value near the "glass transition" temperature. Some confirmation for this view comes from recent work by Turner⁴² who found that by varying the method of specimen preparation T_b values on a particular polythene could be obtained at will between -15° and -69°C . Specimens carefully cut out with a razor gave the lowest values, while specimens roughly stamped out, or abraded, gave the highest. These results suggest that what is really measured is the low temperature notch-sensitivity of the material.

THE PROPERTIES OF MOLTEN POLYTHENE

All methods of fabricating polythene depend on manipulating it in the molten state, and a knowledge of its behaviour as a fluid is therefore of great practical importance. In practice its flow behaviour is found to be markedly non-Newtonian, as is true for many polymers, and no satisfactory theory for it has been evolved. Molten polythene is an elastic fluid, and experiments of the normal type designed to measure viscosity show that the rate of shear is not proportional to the applied shear stress. Hence these experiments do not give a measure of a true viscosity, but of an "apparent viscosity". This considerably complicates the study of fabrication processes, which involve a wide range of shear rates and temperatures. One may look forward, however, to the formulation of a unified descriptive theory as more data become available from laboratory experiments carried out under known conditions.

Physical constants

The crystalline melting point of polythene depends on its molecular structure, as has already been mentioned, but polythenes in general use with densities around 0.92 gm/cc have melting points in the region of $110^\circ\text{--}115^\circ\text{C}$. Parks and Richards⁴³ have studied the effect of pressure on

Table 9.7—THE COMPRESSIBILITY, K , OF MOLTEN POLYTHENE BETWEEN 1 AND 100 ATM.

$T^\circ\text{C}$	$K\ (\text{cm}^2/\text{kg})$ $= \frac{1}{v} \frac{dv}{dP}$
120	8.7×10^{-5}
140	10.0
160	11.6

the properties of polythene up to 160°C and 2,000 atm. They found that the melting point was raised by 2.2°C per 100 atm. pressure. Their values for the compressibility of molten polythene at pressures up to 100 atm. are given in Table 9.7. Raine, Richards and Ryder⁴⁴ have measured the change in heat content (enthalpy) of polythene up to 165°C ;

making use of these data, Parks and Richards have calculated the changes in entropy and heat content with temperature up to 165°C at pressures up to 2,000 atm. These data are relevant to the study of fabrication conditions; for instance, the extrusion of molten polythene approximates to a free expansion process at constant heat content, and such an expansion from 500 to 1 atm. would result in the temperature of polythene rising from 130° to about 145°C.

The specific heat, C_p , of polythene above the melting point was determined by Raine *et al.*,⁴⁴ and later by Dole *et al.*⁴⁵ who found that the dependence on temperature up to 200°C could best be expressed by Equation 10, where T is the temperature in degrees Centigrade:

$$C_p \text{ (cal/gm/°C)} = 0.5859 + 0.000807 (T - 110) \quad (10)$$

Hunter and Oakes⁴⁶ measured the specific volume of polythene at temperatures up to 170°C; a representative value of the specific volume just above the melting point, at about 115°–117°C, was 1.25 cc/gm corresponding to a density of 0.80 gm/cc. Their data give a value for the volume coefficient of expansion above the melting point of about $7.3 \times 10^{-4}/^\circ\text{C}$, while from similar experiments Clash and Rynkiewicz⁴⁷ reported a value of $7.62 \times 10^{-4}/^\circ\text{C}$.

Viscosity and molecular weight

Although the viscosity of molten polythene varies with rate of shear, yet measurements of "apparent viscosity", η^* , at low shear rates of the order of 10 sec⁻¹ have long been used to characterise polythenes and have provided a convenient method of estimating molecular weights. Various methods have been used to measure η^* , depending on the range of values to be covered; the conventional gravity-flow viscometer, the rotational viscometer, the extrusion plastometer and the parallel-plate plastometer.

Flory⁴⁸ was the first to observe a correlation between the melt viscosity of a polymer and its molecular weight. Working with a series of polyesters of relatively low molecular weight ($< 10,000$) he found an exact dependence of viscosity on *weight average* molecular weight, \bar{M}_w , of the form given by Equation 11:

$$\log \eta^* = A + \frac{E}{2.3 RT} + B (\bar{M}_w)^{\frac{1}{2}} \quad (11)$$

E , the activation energy of viscous flow, was practically independent of molecular weight and lay between 8.0 and 8.6 k.cal/mole for all four polyesters studied. It should be noted that these polyesters behaved as Newtonian fluids. The same relation was found to hold for linear and branched polyamides.⁴⁹ Attempts to extend this correlation to other polymers, usually of much higher molecular weight, met with only limited success; in general it was found to be only approximately applicable, and "activation energies" of flow varied with temperature

and with molecular weight, although tending to limiting values at high molecular weights.⁵⁰ Dienes and Klemm⁵¹ working with polythene reported reasonable agreement with Equation 11, but the molecular weights quoted were determined from solution viscosities and were not strictly either weight or number averages. Ueberreiter and Orthmann⁵² used *number average* molecular weights and found deviations from Equation 11 of the type already mentioned; the data tended to be more consistent with the higher molecular weight polymers ($> 30,000$). At a constant temperature, however, these authors found the equation to hold quite satisfactorily, using number average molecular weights. Equation 12 fitted the data at 130°C , and also the data of Maibauer and Myers³⁶ for low molecular weight polythenes;

$$\log \eta_{130^{\circ}}^{*} = -1.54 + 0.035 (\bar{M}_n)^{\frac{1}{2}} \quad (12)$$

the total molecular weight range covered was from 800 to nearly 40,000. A similar correlation, established by Small and Miller¹³ from apparent viscosities determined at 190°C , has been used to correlate melt flow index with \bar{M}_n , as already described.

These equations are empirical, but the analogy between Flory's general equation relating the weight average molecular weight of polyesters to their melt viscosities, and the restricted equation for polythene which contains the number average molecular weight, can hardly be coincidental. However, an explanation of this unexpected parallel must await a deeper knowledge of the dependence on molecular structure of the properties of molten polythenes.

Melt viscosity and elasticity

The outstanding property of molten polythene, which it has in common with many other polymers, is that it is an elastic fluid. This can be demonstrated directly in the type of apparatus used by Hoff⁵³. This was essentially a coaxial viscometer with the molten polymer in the annular space between an outer cylinder and a coaxial plunger, the latter having a torque-free suspension; the outer cylinder was oscillated sinusoidally through a constant small amplitude, and at an appropriate frequency resonance was set up, the plunger amplitude being substantially greater than the driving amplitude. Polythenes with number average molecular weights from 12,000 to 64,000 were studied at frequencies of the order of 20 c/sec and at temperatures up to 230°C ; in most cases their behaviour could be quite well described by a simple Maxwell model, i.e. a spring and "dash-pot" in series. On this basis values of viscosity η , and shear modulus, G , were computed; the latter were found to lie around 10^5 to 10^6 dynes/cm.² The activation energies of melt elasticity and of viscous flow were found to be dependent on molecular weight, decreasing to a common more or less constant value of 3 k.cal/mole at the highest molecular weights.

The above experiments, which were amenable to a very simple analysis, were carried out at very low shear strains, much smaller than those

involved in any practical use of polythene. At high shear strains the behaviour is far more complex. Pollett^{54, 55} has investigated strain recovery from continuous shear and found elastic effects to persist at very high strains, of the order of 10,000; Dexter⁵⁶ came to similar conclusions from a study of the time-dependence of shear strain on shear stress. It is the purpose of much current work in this field to devise appropriate experimental and theoretical techniques for the study of these visco-elastic effects in terms of separate elastic and viscous components of stress and strain, and to correlate these with molecular structure.^{57, 58}

Apparent viscosity as a function of shear rate

A convenient method of measuring apparent viscosity, under conditions which approximate to those obtaining in fabricating equipment, is to measure the volume rate of extrusion, Q , as a function of pressure, P , using an extrusion plastometer with a cylindrical die. The apparent

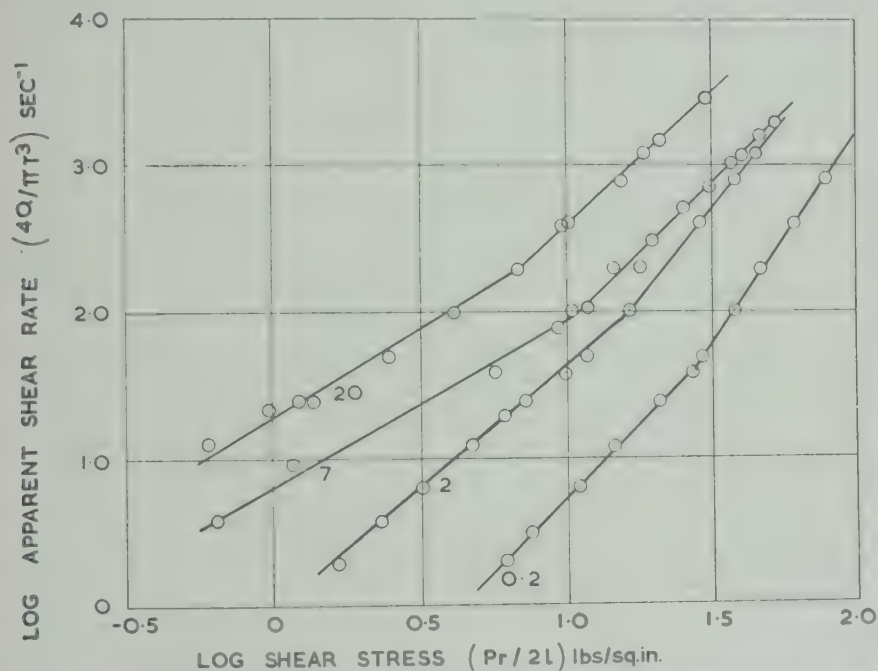


Fig. 9.23. Extrusion of polythene through a cylindrical die: dependence of shear rate on shear stress at 190°C for polythene of M.F.I. 0.2, 2, 7 and 20

viscosity is the ratio of maximum shear stress, $Pr/2l$, to shear rate, $4Q/\pi r^3$, where r and l are respectively the radius and length of the die. The non-Newtonian nature of polythene is shown by the fact that the value so obtained for the apparent viscosity, η^* , is not constant but depends on shear rate. Equation 13 gives the form of the dependence:

$$\frac{Pr/2l}{4Q/\pi r^3} = \eta^* = \frac{\text{Constant}}{P^{(\alpha-1)}} \quad (13)$$

this shows that the apparent viscosity decreases with increasing shear stress, as the exponent α is greater than unity. For ordinary polythenes

with densities of about 0.92 gm/cc α lies between 1.5 and 2.0 at about 190°C, decreasing at higher temperatures. Alternatively the actual relation between shear rate and shear stress, which are proportional to Q and P respectively, may be expressed as in Equation 14:

$$Q = \text{Constant} \times P^\alpha \quad (14)$$

this shows that experimental data can be conveniently presented in the form of a double logarithmic plot of shear stress *v.* shear rate, which should give a straight line of slope α . Some data obtained by Clegg and Hoff⁵⁹ illustrating the effects of molecular weight (M.F.I.) and temperature are summarized in this way in Fig. 9.23 and 9.24. The interesting features of these plots are the discontinuities, corresponding to a sudden

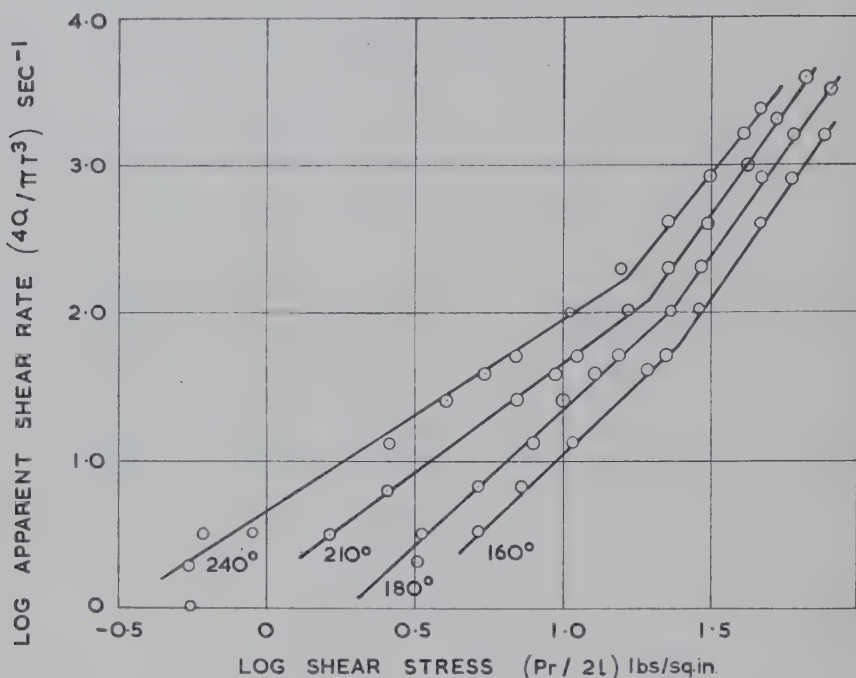


Fig. 9.24. Extrusion of polythene of M.F.I. = 20 through a cylindrical die: dependence of shear rate on shear stress at 160°, 180°, 210° and 240°C

increase in the value of the slope α , above a critical shear rate. These discontinuities also mark in many cases the appearance of irregularities on the surface of the extruded polythene; it would appear that the mechanism of flow changes at this point. This view has also been put forward by Westover and Maxwell⁶⁰ on the basis of similar work, although it is difficult to accept the interpretation offered in terms of a critical Reynolds number; the calculated Reynolds numbers, of the order of 10^{-4} , are many orders of magnitude smaller than is usually accepted as indicating the onset of turbulence. It is more probable that the phenomenon is a function of the elasticity of the melt, and is associated with the long-chain nature of the flowing molecules; it is likely, for instance, that such factors as flow orientation and shear heating are involved. This sort of behaviour is exhibited by other polymers. Thus polystyrene filaments extruded at high shear rates have been observed to assume a

regular helical form, suggesting a dynamically stable if abnormal state of flow.⁵⁸

The temperature dependence of apparent viscosity can be calculated from the data given in Fig. 9.24, and an "activation energy" derived. However, the value obtained depends on whether the calculation is based on data at constant shear stress or at constant shear rate, and also varies with these parameters; the values range from 4 to 17 k.cal/mole. Similar, if not so marked, discrepancies are revealed by a comparison of other published data: 11 k.cal/mole quoted by Spencer and Gilmore,⁶¹ and 11.3 to 13.2 k.cal/mole by Pollett;⁵⁵ 6 to 7 k.cal/mole derived from other data given by Pollett,⁵⁴ and 9.1 k.cal/mole quoted by Tordella.⁶² Yet other values for the activation energy are obtained if the melt elasticity and melt viscosity are separately determined, as has been attempted by Hoff⁵³ and other workers.^{56, 57} It is apparent from this state of affairs that the flow behaviour of molten polythene cannot be explained by any simple theory of visco-elasticity, and that empirical equations must be used with caution if it is desired to predict from them the flow behaviour of polythene under conditions other than those used to obtain the equations.

POLYMETHYLENE AND HIGH DENSITY POLYTHENE

Polythene, made by the high temperature, high pressure polymerization of ethylene, is a branched polymer. The linear polymer with the same stoichiometric formula, viz. $(CH_2)_n$, can be made by the catalytic decomposition of diazomethane, and has been designated "polymethylene" to emphasize its essentially linear structure.

Polymethylene has been something of a laboratory curiosity, but its properties are of interest in that this polymer represents an extreme member of the polythene family, and also its structure is probably very similar to that of the recently discovered "high density" polythenes. These polymers, made by the polymerization of ethylene under special conditions, are highly crystalline. Substituted polymethylenes, in which side groups of known length have been introduced into the molecule, have also been made and these may be considered as rather crude models of ordinary polythene.

Polymethylene

Although the formation of solid paraffinic compounds from diazomethane had been noted as long ago as 1900, Leitch and Cambron^{3, 4} were probably the first workers to make high molecular weight materials in reasonable yield; these authors used copper powder as a catalyst. Using the same procedure Buckley, Cross and Ray⁵ prepared polymethylene of estimated molecular weight 20,000 with a melting point of 135°C, highly crystalline and brittle. Subsequently Buckley and Ray⁶ obtained better yields of polymethylene of much higher molecular weight using trimethyl borate, BF_3 and similar catalysts. A study of the melting behaviour of polymer prepared in this way was made by Mandelkern

et al.;⁸ they found the melting point to be 136–137°C, and the melting range to be very much narrower than for polythene: about 70% of the crystalline regions melted within 4°C of the temperature of final disappearance of crystallinity. This more uniform melting behaviour, and the higher melting point, must be attributed to the greater perfection of the crystallites arising from the completely linear chain structure. For the same reason these polymethylenes are much more crystalline than polythene; thus polymethylene as made, and not processed in any way, has been found to have a density as high as 0.98 gm/cc and to be 89% crystalline as estimated from x-ray examination.⁶³ This high crystallinity is also reflected in the lower solubility of these polymers, some being only swollen in boiling toluene.

Polymethylene differs from polythene in another way, which seems to be typical of very highly crystalline polymers, in that it can be obtained much less crystalline by “quenching”, i.e. by cooling the polymer rapidly from the molten state. In fact it requires a lengthy high temperature annealing treatment to raise the density of a moulding to a value approaching that of the original polymer as made; an ordinary moulding may have a density of 0.94 gm/cc and be only about 60–70% crystalline.⁶³ This is a factor which considerably complicates the study of the physical properties of polymethylenes, since these will certainly depend on the degree of crystallinity of the specimens. Nevertheless, there is no doubt that polymethylene is stiffer and stronger than polythene, and that it is tough and flexible down to low temperatures if of high molecular weight. Kantor and Osthoff⁷ report a tensile strength of 4,900 lb/sq. in. with an elongation of 500% measured on specimens cut from moulded sheet, and the density of this sheet was only 0.938 gm/cc.⁶⁴ Working with material which had a similar density when moulded, Turner⁶³ obtained very variable results for ultimate tensile strength and elongation, with values widely scattered above and below 5,000 lb/sq. in. and 200% respectively, depending on the state and form of the specimens and on the speed of testing. When subjected to a low temperature brittleness test no specimens broke at –74°C. This polymethylene probably had a very high molecular weight since its melt viscosity at 190°C was about 10^7 poise, equivalent to a M.F.I. value of about 0.007; this may well have been the reason for its good flexibility, even at low temperatures, compared with the polymethylenes described by Buckley *et al.*⁵ which were of relatively low molecular weight and brittle.

Relatively little has been published about the properties of substituted polymethylenes. Buckley *et al.*^{5, 6} studied the effect of increasing numbers of methyl side groups on the nature of the polymers; they were made from mixtures of diazomethane with varying amounts of diazoethane. The polymer with about 3 methyl side groups for every 100 carbon atoms ($\text{Me}/100.\text{C} = 3$) was quite similar to polythene: its density was between 0.92 and 0.93 gm/cc; it was about 60% crystalline and soluble in boiling toluene. With increasing $\text{Me}/100.\text{C}$ ratio, the polymers became more flexible and soluble at lower temperatures; polymers with $\text{Me}/100.\text{C} > 20$

were soluble in chloroform in the cold, and were only about 5% crystalline. Similar changes were observed on introducing longer side-chains, such as *n*-amyl ones. Polymers which may be considered as extreme examples of substituted polymethylene are polyethylidene and polypropylidene, i.e. polymers with every chain carbon atom carrying a methyl or ethyl group respectively. These polymers are brittle, amorphous, glassy solids, soluble in ether, and softening in the region of 80°–100°C.^{4, 5}

*High density polythene*⁶⁵

Polymers of this class are a recent development. Their properties are therefore only known in outline and this account of them must be considered as a preliminary qualitative description. In the first place there is no doubt that these polythenes have substantially the same linear, unbranched molecular structure as the polymethylenes already referred to. They do not seem to be quite so highly crystalline as polymethylene, as judged by their densities which lie between 0.93 and 0.96 gm/cc; this may be a real reflection of minor imperfections in their molecular structure, or it may in part be associated with the "quenching" phenomenon which was noted above in connection with polymethylene. Both factors are probably operative: the influence of the former is to be seen in their crystalline melting points, quoted as lying between 123° and 132°C, which are rather lower than that of polymethylene. However, these values are still considerably higher than the melting point of low density polythene.

The high density polythenes at present under development have M.F.I. values lying between 0.1 and 6.0, the lower limit being set by the inability of processing equipment to deal with materials of high viscosity and the upper limit probably being determined by the deterioration in mechanical properties with decreasing molecular weight. It is not possible to state what molecular weights these polymers have since it is most unlikely that the relation between M.F.I. and number average molecular weight found earlier for polythene would be applicable; however, data reported by Schulz and Mehnert⁶⁶ indicated that a high density polythene of M.F.I. = 0.4 had a *weight average* molecular weight of about 90,000 as determined by the light scattering method. It is probable that the molecular weights of these polythenes are in fact quite high since they are reported as having good low temperature flexibility and resistance to environmental cracking.

The stress-strain curves of high density polythenes are qualitatively similar to those given by ordinary polythenes (cf. Fig. 9.2); however, such data as are available indicate that their behaviour shows the same sort of complicated dependence on the conditions of test as does that of polymethylene. In particular, ultimate tensile strength and elongation at break are very dependent on the speed of testing; this is illustrated by the data given in Table 9.8 which were obtained on injection moulded specimens.^{65a} This is probably one of the reasons why tensile strengths between 2,800 and 5,500 lb/sq. in. have been reported, although the

POLYTHENE

Table 9.8—TENSILE PROPERTIES OF HIGH DENSITY POLYTHENE AS A FUNCTION OF RATE OF EXTENSION

(Specimen gauge length approx. 2 in.)

Rate of extension, inches/minute	Ultimate tensile strength, lb/sq. in.	Elongation at break, %
1	3600	320
5	4400	150
10	4700	80
15	4700	60
20	4600	30

possible effects of "quenching" must not be overlooked, nor the likelihood of real differences between these polythenes from different sources. Thus one type is unusual in having an elongation at break of about 1,000%, even at a quite high rate of extension.^{65c} From the practical point of view, the quantities of most interest are the stress and strain at the yield point; at room temperature the former is in the region of 2,800–3,600 lb/sq. in., and the latter around 15%. The only extensive work so far published is that of Schulz and Mehnert⁶⁶ who included in their investigation the temperature dependence of tensile properties. On the particular material used, the yield stress fell nearly uniformly with rising temperature from about 2,800 lb/sq. in. at 20°C to 700 lb/sq. in. at 100°C. These authors, in addition to noting the effects of speed of testing, observed a dependence of ultimate tensile properties on specimen dimensions. Even at this early stage it is apparent that the behaviour of high density polythenes is at least as complicated as that of the conventional polythenes, if not more so.

DYNAMIC MECHANICAL PROPERTIES

The dynamic mechanical properties of high polymers are being increasingly studied, not only because it is of practical importance to know how polymers behave when stressed at different rates and in different ways, but also and perhaps primarily because the data obtained should in principle be amenable to theoretical analysis in terms of fundamental constants; a knowledge of these constants for a polymer would in theory permit one to calculate its response to any kind of stress, and furthermore one might expect some kind of correlation between the values of the constants and the structures of different polymers.⁶⁷ The subject however is as yet in its infancy, both with respect to the experimental data available and the development of techniques of theoretical analysis. This applies particularly to polythene, which is not one of the more studied polymers, and which presents the additional complication of being crystalline.

Techniques of investigation

The parameters which can be measured in a general study of mechanical behaviour are stress, strain, temperature and time; in most conventional

tests the time parameter is not very closely defined, and is usually obtained only as an integral value over a range of values of stress and strain. It is the purpose of dynamic tests to obtain stress-strain data to which definite values of the time parameter can be assigned. In practice the most convenient way of doing this is to measure the response to stresses or strains applied at a definite *frequency*; this may be done in a dynamic system in which free or forced vibrations are set up in a specimen in shear, flexure or compression, or one may study the propagation of stress waves in a suitable specimen. The former method is the one most commonly used, and the most convenient for moderate and low frequencies; the latter is only suitable for work at high frequencies. A convenient way of summarizing the data for comparative purposes, however obtained, is to quote values for modulus and internal friction as functions of temperature and frequency. Polymers are not ideal elastic solids; when subjected to mechanical vibrations, part of the elastic energy imparted to the specimen is dissipated as heat, and this phenomenon is known as internal friction. Internal friction, or "mechanical losses", can be simply defined as the ratio $\Delta W/W$, where ΔW is the energy dissipated in a stress cycle and W is the elastic energy stored in the specimen when the strain is a maximum. Various other definitions are in use, all of which lead to quantities proportional to $\Delta W/W$. It is unfortunate that, to get values of modulus and mechanical losses over a wide range of frequency and temperature, it has been necessary to resort to several different experimental techniques, each suitable only for a limited range of conditions. Difficulties arise therefore in correlating the data and in reducing them to comparable functions; for instance, experiments in torsion give values of shear modulus G , whereas experiments on vibrating cantilever specimens give values of Young's modulus E . When comparing such data on polymers it is usual to assume that $E = 3 \times G$, i.e. that Poisson's ratio is 0.5. The subject of internal friction, its definition, its mechanism and methods of measurement, has recently been reviewed by Kolsky.⁶⁸

Data for polythene have been obtained by several workers covering in each case a limited range of temperature and frequency: Philippoff⁶⁹ reported data obtained in forced flexural vibrations at low frequencies between 10^{-5} and 10 c/sec from -23°C to $+73^{\circ}\text{C}$: Lethersich^{70, 71} measured shear modulus and losses in torsion from 10^{-4} to 300 c/sec at 20°C : Nielsen⁷² used a torsion pendulum technique in the frequency range 0.2 to 1 c/sec from 25°C to the melting point, to determine shear modulus and losses of six polythenes of widely different degrees of crystallinity, while Nielsen and Buchdahl⁷³ using the same technique reported data over a rather smaller temperature range on a commercial polythene: Schmieder and Wolf⁷⁴ used a similar technique at 1 to 10 c/sec and from -160° to $+100^{\circ}\text{C}$: Dunell and Dillon⁷⁵ working with single filaments of polythene excited in longitudinal vibration worked in the frequency range 10 to 100 c/sec at 21°C (70°F): Hillier⁷⁶ used a vibrating cantilever method between 35 and 80 c/sec at 30° and 40°C : Robinson^{77, 78} used

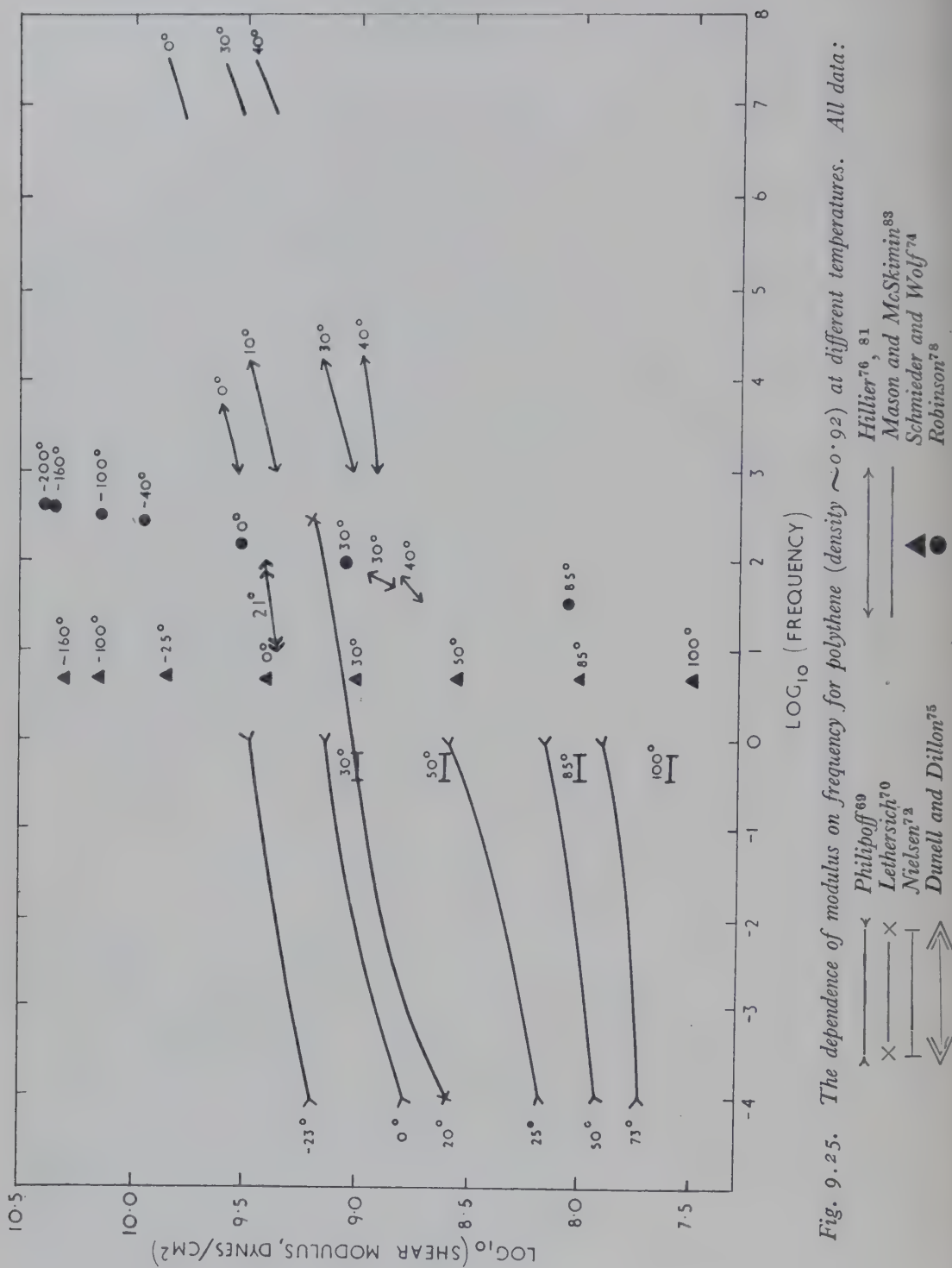


Fig. 9.25. The dependence of modulus on frequency for polythene (density ~ 0.92) at different temperatures. All data:

the same principle operating from 20 to 1,000 c/sec and between -250° and $+100^{\circ}\text{C}$: Hillier⁷⁹ covered the frequency range from 1 Kc/sec to 16 Kc/sec between 0 and 40°C using an apparatus in which longitudinal oscillations were propagated in polythene monofilaments, and using the same technique Hillier and Kolsky⁸⁰ and Hillier⁸¹ studied the effect on the dynamic mechanical properties of stretching the monofilament: McSkimin⁸² and Mason and McSkimin⁸³ used a pulse technique to make measurements in the range 5 to 50 Mc/sec between 10° and 70°C . In the work referred to above, the measurements were carried out at very low strain amplitudes, the intention being to work in the most nearly linear region of the stress-strain curve. In a rather different type of experiment Kolsky^{84, 85} has measured the dynamic stress-strain curve up to 20% strain in compression on a time scale of about 20 to 30 μ sec using a pulse technique; he also studied the attenuation of large amplitude pulses propagated along polythene rods. The various authors quoted have not given in all cases full details of the polythenes used in their experiments, but it may be presumed that they were typical of commercially available materials, i.e. with densities ~ 0.92 gm/cc and M.F.I. values between 2 and 20; in a few instances work has been done on polythenes of higher density and on polymethylene.^{72, 78, 86}

It is customary to include in the classification of dynamic mechanical properties the study of stress relaxation, in which decay of stress as a function of time is measured, the strain being maintained constant. This may be considered as the inverse of the study of creep behaviour in which extension is measured as a function of time under (in the ideal case) constant stress. All these dynamic properties are inter-related, and in principle full knowledge of one set of properties would permit prediction of the others. Stress-relaxation studies on polythene have been reported by a few workers^{75, 80, 87, 88} but the data are rather fragmentary. The subject is outside the scope of this discussion, but has been considered by Alfrey,⁶⁷ Kolsky⁶⁸ and others.^{89, 90, 91, 92}

The interpretation of experimental results

The data available from dynamic mechanical measurements, in the form of values of modulus and mechanical losses, cover nearly twelve decades on the frequency scale and a temperature range of 300°C , but the amount of detail is too meagre to permit other than rather general and qualitative conclusions. Fig. 9.25 shows the modulus data, converted where necessary to shear modulus, plotted on a logarithmic scale against log (frequency). It is clear that at all frequencies the modulus falls with rising temperature, the extreme range of values being $\sim 10^3$. At any given temperature, the modulus falls with decreasing frequency but less markedly; over the frequency range of 10^{12} , the modulus falls by a factor of perhaps 40. Considering the variety of methods used to obtain these results, and the fact that only in a few instances did different workers use specimens made from the same sample of polythene, the consistency of the data is quite reasonable. There are a few rather large discrepancies:

the modulus values quoted by Dunell and Dillon⁷⁵ appear to be rather high, but this might be accounted for if the filaments they used were oriented; and the modulus values found by Philippoff⁶⁹ are all rather low compared with those found by other workers. The apparent discontinuities between different sets of data may conceal real inflexions but it would be dangerous to infer very much from this evidence alone other than the difficulty of obtaining truly comparable results using different experimental techniques. More interesting information can be obtained from a study of self-consistent data, all obtained by the same

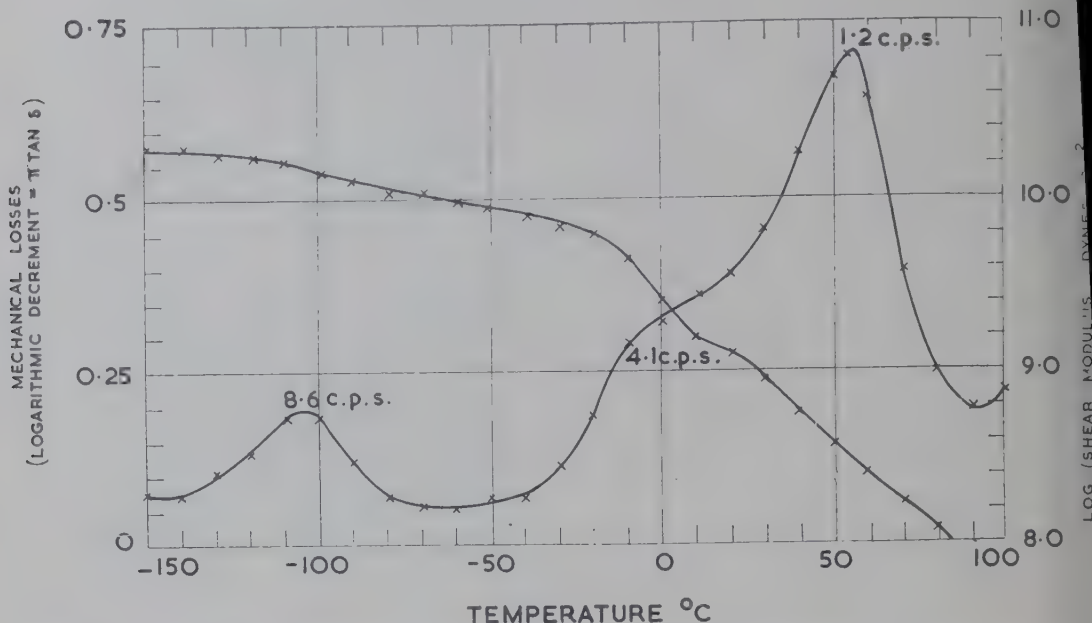


Fig. 9.26. The dependence of shear modulus and mechanical losses on temperature for polythene at 1-10 c/sec: Schmieder and Wolf⁷⁴

method, showing the precise way in which the modulus and the associated mechanical losses vary with temperature. Fig. 9.26 shows the data of Schmieder and Wolf⁷⁴ obtained at about 5 c/sec, and Fig. 9.27 the data of Robinson⁷⁸ measured between 50 and 200 c/sec; both show the same general features. The decrease of modulus with rising temperatures is not uniform; there are three temperature regions where it is rather more rapid, and in these regions the mechanical losses show maxima.

These "dispersion regions" of the modulus, with associated maxima in the mechanical losses, are quite analogous to the better known dielectric phenomena (also shown by polymers), where a maximum in dielectric losses is associated with a rise in dielectric constant with increasing temperature. The analogy is probably very close, even to the extent that the movement of definite groups of atoms in the polymer molecule may be associated with the mechanical dispersions in the same way that dielectric dispersions may be associated with the interaction of specific dipoles with the applied electric field. One may therefore hope to find a direct correlation between the dynamic mechanical and dielectric behaviour of polymers; there is evidence for this in several in-

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stances,^{93, 94, 95, 96} and some data for polythene have been reported by Robinson and Oakes.⁹⁷ The molecular mechanisms responsible for this correspondence between dielectric and mechanical behaviour are by no means fully understood, but they can at least be semi-quantitatively described in terms of rate process theory.^{67, 68} The basic assumption is that a long chain molecule may be treated as an assembly of a very large number of a few distinct kinds of atomic groupings, or segments, joined together in a regularly repeating pattern; in the simplest case all the segments are identical, but in general there will be two or more kinds of segment. Each segment is capable of thermal oscillation (or "micro-Brownian" movement) in a potential energy well characteristic of its nature and its environment, the amplitude and frequency of oscillation being a function of the structure and mass of the segment and of the temperature. The response of a segment to a dynamic stress field will then be a function of the applied frequency and temperature. At very low temperatures or very high frequencies no segment will be able to respond. They will all be effectively "frozen in" and will be unable to make any contribution to the compliance of the polymer; the numerical

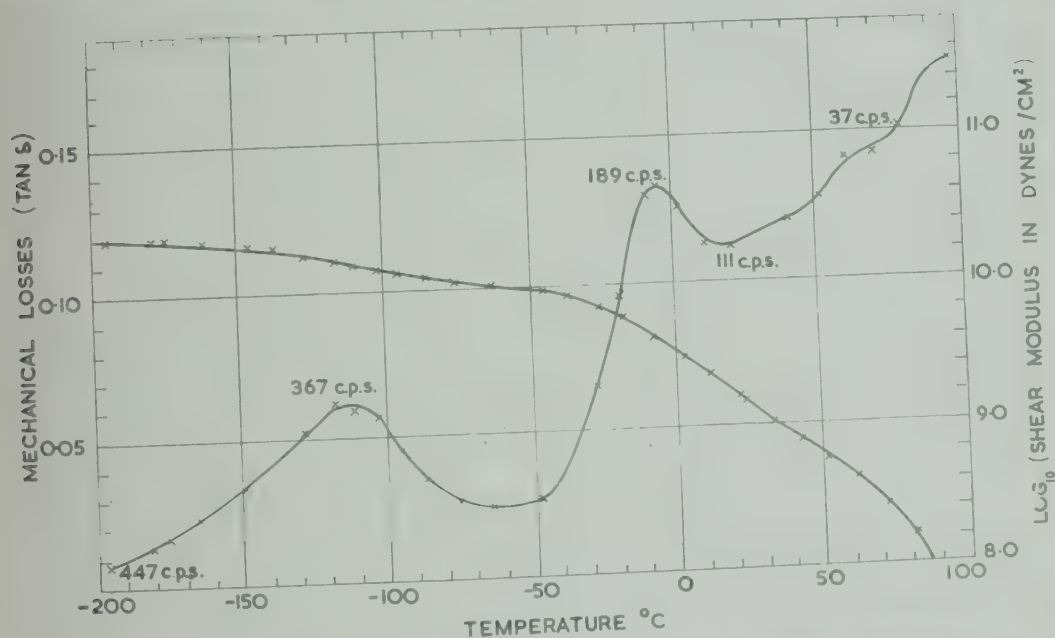


Fig. 9.27. The dependence of shear modulus and mechanical losses on temperature for polythene at 30-450 c/sec: Robinson⁹⁸

values of modulus and losses will be determined by other factors such as the thermal properties of the polymer and the compliance of valency bonds. With increasing temperature or decreasing frequency a stage will be reached where segments of a particular kind begin to respond to the applied field. Owing to frictional forces which cannot be accurately specified but which are akin to viscous forces, energy is absorbed and dissipated as heat; at the same time the increasing compliance is noted as a drop in modulus. At even higher temperatures or lower frequencies

the segments respond to the applied field with no hysteresis and the losses fall again while the modulus remains constant at its lower value, until a stage is reached where another kind of segment begins to interact with the field resulting in a second "dispersion region". This is a highly idealized and simplified picture, but it does illustrate how mechanical behaviour can be directly related, at least in theory, to features of molecular structure; and it also shows how it can come about that time (i.e. frequency) and temperature are equivalent parameters in determining the response of polymers to applied stresses and strains. This latter concept is commonly accepted in qualitative terms, and is made use of quantitatively in the analysis of stress-relaxation and creep data.

It is also implicit in this picture of the molecular basis of the mechanical behaviour of polymers that in crystalline polymers it is the amorphous regions which really determine the response of the material to applied stresses. The segmental mobility thought to be responsible for the dispersion phenomena must be impossible in an ordered crystalline lattice. The crystalline regions act as "reinforcing units" which raise the level of modulus values and perturb the behaviour of the polymer by their indirect effect on the structure of the amorphous regions. This picture requires qualification however in three respects, all very relevant to the case of polythene. First, gross changes in mechanical properties occur with change of temperature in the region of crystalline melting which is very wide for polythene, and this effect largely determines its behaviour above about 50°C. Secondly, the level of mechanical properties if not their dependence on time and temperature will clearly be dependent on degree of crystallinity even below the melting range, an effect which is very important when comparing different samples of polythene, as has already been noted. And thirdly, all these considerations apply to properties measured at very small strains; a variety of complicating effects operate at large deformations, especially with crystalline polymers.

With this conception of the molecular basis of polymer properties, and by analogy with the behaviour of other polymers, it is possible to present a qualitative explanation of the dynamic mechanical properties of polythene, and to indicate the connection between these and other properties of polythene. Referring to Fig. 9.26 and 9.27 the low temperature dispersion in the region -100° to -120°C is probably associated with the movement of chain segments consisting of a few $-\text{CH}_2-$ groups; it is in this temperature region at the particular frequencies used that they acquire limited mobility. This interpretation is supported by the fact that other polymers of quite different structure but containing short runs of $-\text{CH}_2-$ groups also show this type of low temperature "transition", e.g. polymers of aliphatic esters of methacrylic acid⁹⁸ and polyhexamethylene adipamide.⁷⁸ The dispersion region or transition around -10°C seems to be associated in some way with the short side chains and branch points in polythene; it is absent, or very much depressed, in the linear polymethylenes. This point is illustrated by the data obtained by Robinson⁷⁸ on polymethylene, which are shown in

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Fig. 9.28 for comparison with the polythene data in Fig. 9.27. As it occurs at a higher temperature, the segments involved in this transition presumably are larger and comprise more atoms than are involved in the low temperature transition. The transition which sets in at about 50°C is almost certainly of a rather different nature, and due to molecular rearrangements in the amorphous regions brought about by the crystalline melting process which is known to set in at about this temperature.

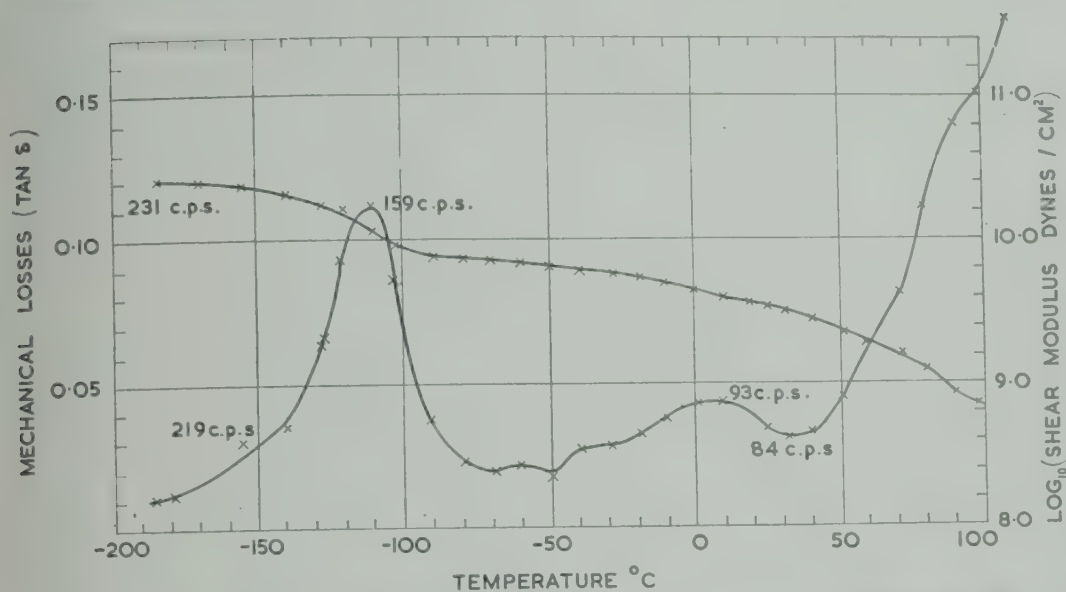


Fig. 9.28. The dependence of shear modulus and mechanical losses on temperature for polymethylene at 80–250 c/sec: Robinson⁷⁸

This transition is almost independent of frequency. A reasonable interpretation of this fact would be that as the crystallites melt the amorphous regions become less constrained and much larger segments of the molecules become free to move; as this happens at a high temperature, these segments will respond to both low and high frequencies, and hence the transition appears to be sensibly independent of frequency. An additional effect, which will be quantitatively very large, will be a drop in modulus due simply to the disappearance of the crystallites considered as reinforcing units. The transitions at lower temperatures, considered as rate processes, would be expected to be frequency dependent, and in fact estimates of their activation energies have been made. Robinson⁷⁸ estimated a value of about 6 k.cal/mole for the lowest transition, and 30 k.cal/mole for the intermediate one, as determined in the frequency range 50 to 1,000 c/sec.

From the phenomenological point of view alone, the correlation between the dynamic mechanical and dielectric properties of polythene indicated by the results of Robinson and Oakes⁹⁷ is of great interest. Combining both types of data it is possible to construct a coherent picture of the frequency and temperature dependence of the transitions in polythene, which is reasonably consistent with the dynamic mechanical data

of Fig. 9.25 but which could not have been deduced from them. Thus, Fig. 9.29 summarizes in a schematic, semi-quantitative manner the dependence of the shear modulus, G , of polythene (density ~ 0.92) on temperature and frequency. The actual values of shear modulus have been chosen with reference to Fig. 9.25; the loci of the transition regions have been based on the dynamic loss data of Robinson⁷⁸ and of Schmieder and Wolf,⁷⁴ and on dielectric data obtained by Reddish and Oakes.⁹⁹ The transitions have been accentuated somewhat to make them more readily seen, but the general picture is probably a fair approximation to the truth.

There are several interesting features about Fig. 9.29 which are worth noting, although conclusions must necessarily be rather tentative. In the

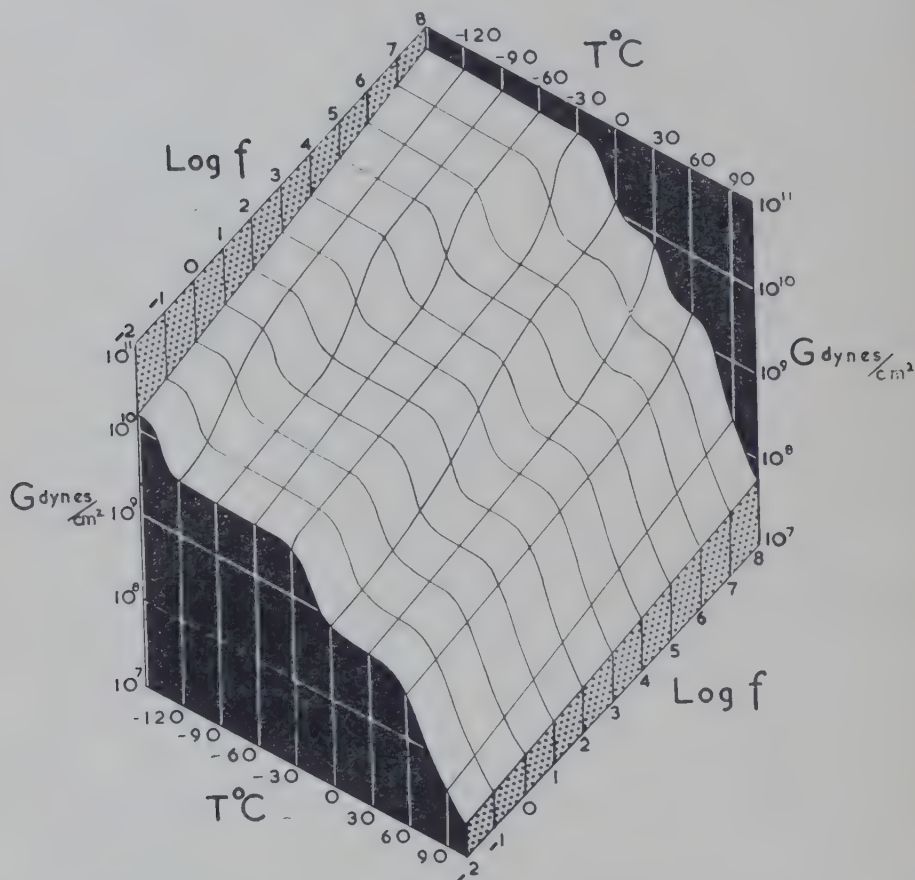


Fig. 9.29. Approximate dependence of shear modulus, G , of polythene on temperature and frequency

first place, the temperature intervals between transitions decrease with increasing frequency as a consequence of their different activation energies; at high temperatures and frequencies all the transitions merge, as has been noted with other polymers.⁹⁵ The other point of interest is the frequency dependence of the lowest temperature transition. At low and moderate frequencies it is around -120°C , but at 100 Mc/sec it sets in just below 0°C . There is some indication of this in the data obtained by Mason and McSkimin,⁸³ and it seems probable that they would have

found that transition (as a large rise in modulus) if measurements had been extended from 0° to about -30°C (cf. Fig. 9.25). At even higher frequencies this transition should be around room temperature, and should theoretically be detectable by dielectric loss measurements in the centimetre waveband on slightly oxidized polythene, the technique used by Oakes and Robinson.⁹⁷ However these authors found that in their dielectric experiments the intermediate temperature transition was the dominant one, and this transition might well be merging with the low temperature one at these frequencies ($\sim 3 \times 10^{10}$ c/sec) which would rather confuse the situation. It does nevertheless appear that the rather uninteresting data of Fig. 9.25 do in fact relate to a most interesting set of properties and that much more experimental work is needed to establish their true interdependence.

The significance of "transitions"

From the practical point of view dynamic mechanical studies are of interest in that they should provide a general picture of the mechanical behaviour of polythene within which it should be possible to see correlations between the properties of polythene measured in more conventional ways. This approach also reveals certain difficulties of definition and terminology, of which the most outstanding example is the definition and meaning of the property "second order transition", or "glass transition".

Flory¹⁰ has recently discussed the nature of transitions observed in high polymers and has pointed out that the term "second order transition" should be abandoned completely. He distinguishes between two kinds of transition in polymers, melting transitions which occur in crystalline polymers when the crystallites melt, and glass transitions which occur as the result of freezing-in of disorder as the temperature is decreased in amorphous polymers and in the amorphous regions of crystalline polymers. Amorphous polymers must be considered as liquids of very high viscosity which readily pass into a glassy state on cooling through a critical temperate zone. Below the glass point, the liquid is not in its thermodynamically most stable state, yet certain thermodynamic relations may be developed and applied to the glassy state. These considerations provide a satisfactory and consistent basis for the interpretation of the behaviour of polymers showing just one simple glass transition, but recent work has shown that many polymers show more than one transition located in the amorphous regions. This does not of course in any way invalidate the arguments developed, in that it is not unreasonable to find disorder in a complex structure frozen-in progressively over different temperature regions. It does however raise the questions: where there are two or more transitions, is there any justification for describing one of them as *the* glass transition? if so, what is the criterion to be?

These are new questions in polymer physics which have hardly been recognized yet as being meaningful. It might be thought that the transition occurring at the lowest temperature should be designated *the* glass

transition but this definition would certainly be unacceptable if applied to the polymers of methacrylic esters.^{95, 98} The definition favoured by the author is that the term glass transition should be reserved for that transition at which *all* the different kinds of segment comprised in the main polymer chain (if in fact there is more than one kind) have acquired mobility. This means of course that with some polymers it may not be possible to label the glass transition with certainty without undertaking a considerable investigation, and polythene is one of these. There are however some general considerations which should permit unambiguous definition with most polymers.

In the first place, for purely amorphous polymers such as polystyrene, polyvinyl chloride, polymethacrylic esters, etc., the glass transition as defined above is the highest temperature transition, this being the temperature at which the rigid, glassy solids collapse to very viscous liquids. It is fairly certain that this must be the temperature at which the main polymer chains become mobile. Transitions at lower temperatures when they occur, are associated with side group segments or other structural features which largely determine the rigidity of the glass immediately below the glass transition.^{95, 98} The situation is more complex with crystalline polymers since the highest temperature transition is a melting transition and the amorphous regions retain an artificially imposed stability up to the actual crystalline melting point, thus permitting in principle the manifestation of transitions in the amorphous regions at temperatures between the glass transition and the melting transition.

It is not possible therefore to identify the glass transition in a crystalline polymer without additional information. If a crystalline polymer can be obtained wholly amorphous by rapid cooling from the molten state, then the temperature at which the amorphous polymer starts to crystallize is a fair indication of the glass transition temperature, T_g , in that crystallization must involve movement of all segments of the main chain. This is one line of evidence for setting T_g at about 70°C for polyethylene terephthalate.¹⁰⁰ This criterion can only provide negative, but not unimportant, evidence in relation to polythene since there have been no reports of polythene ever having been obtained wholly amorphous. Attempts to do so, or even to vary the proportion of crystalline material, by quenching molten polythene at -80°C or at lower temperatures have always failed. This suggests that the segments of -CH₂- groups in the main chain are mobile down to very low temperatures. A comparison of the behaviour of polythene with that of polymers for which T_g is better known leads to the same conclusion. This is all consistent with the interpretation given above, that the lowest temperature transition in polythene is associated with the movement of segments consisting of -CH₂- groups, i.e. is *the* glass transition in the sense defined here. It is interesting to note that the low temperature transition associated with the chain of -CH₂- groups in, for instance, polybutylmethacrylate, is not the glass transition for that polymer because the CH₂ groups are in side chains and not in the main chain.⁹⁸

This identification of the glass transition in polythene with the lowest temperature dynamic mechanical transition has been assumed in the discussion of the general mechanical properties of polythene given earlier. It has been used to interpret the temperature dependence of the tensile properties of different polythenes, and is a reasonable explanation of the excellent low temperature properties of polythene.

Some correlations of physical properties

The effect of crystallinity in polythene is seen to be in some senses only secondary, although from a practical point of view it is of the greatest importance. At temperatures above about 50°C , changes in degree of crystallinity with temperature really determine its mechanical behaviour, and the crystalline melting point and melting range determine the upper temperature limit of practical use. Below 50°C down to moderately low temperatures, the degree of crystallinity of polythene sets the *level* of mechanical properties, e.g. modulus, but it is the properties of the amorphous regions which largely determine the way in which these properties vary with temperature. At very low temperatures, in the region of the glass transition at about -120°C , the degree of crystallinity becomes almost unimportant and the properties are dominated by the now glassy amorphous regions. This may be illustrated by comparing the shear modulus values for polythene and polymethylene from Fig. 9.27 and 9.28. Although polythene has a lower modulus at room temperature, below about -150°C they both have the same shear modulus of about 2.3×10^{10} dynes/cm² ($\log G = 10.4$). This is also the interpretation suggested to account for the convergence of the tensile moduli at low temperatures for the different polythenes shown in Fig. 9.11.

These considerations also indicate why it is that in any tensile experiment the tangent modulus at the origin as measured from a stress-strain curve must be to some extent indeterminate, however sensitive and accurate the measurements may be. The smaller the time interval from zero over which the modulus is in effect measured, the higher the effective frequency of the experiment, and we know from the dynamic mechanical data that the modulus increases with increasing frequency. The smallest time interval in which a measurement can be made is set by the limitations of actual tensile testing machines, and this may be the limiting factor determining the gap between the origin of the stress-strain curve and the first experimental point of any significance.

The difficulty in fact is that a modulus value to be truly meaningful must be quoted together with its appropriate time interval, or effective frequency, and it is not possible to do this accurately for a tensile modulus. One can, however, make an estimate and by this means compare tensile data with dynamic mechanical measurements. For example, values of E_0 , the tangent modulus at the origin, are given in Fig. 9.10 for polythene B. At 0°C $E_0 = 10^5$ lb/sq. in., which is equivalent to a value for the shear modulus, G , of 2.3×10^9 dynes/cm²; or $\log G = 9.36$. Now the value of E_0 was computed in effect from the stress-strain curve up to 0.1

to 0.2 % strain, which at a rate of extension of 190 % per minute means on a time scale of about $\frac{1}{16}$ to $\frac{1}{32}$ of a second. The equivalent frequency is therefore probably somewhere between 10 and 50 c/sec. These values, $\log G = 9.36$, $T = 0^\circ\text{C}$, $\log f = 1.17$, are quite consistent with the dynamic mechanical data as may be seen from Fig. 9.25, 9.26 and 9.27.

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CHEMICAL PROPERTIES

W. L. THORNE

COMPARED with many other plastics polythene is unusual in its insolubility and in its inertness to a wide range of chemical agents. The material has a chemical resistance which is complementary to that of metals.¹ Thus polythene is resistant to attack by inorganic acids, alkalis and aqueous solutions which cause corrosion of metals. Organic solvents, on the other hand, which may affect polythene, usually have little if any effect on metals.

At room temperature, polythene is almost completely insoluble in all organic solvents though some absorption, softening or embrittlement may occur. At temperatures above 70°C (158°F) low density polythene dissolves in a number of common solvents, for example, xylene, toluene, amyl acetate, trichlorethylene, paraffin and turpentine. It is not dissolved by glycerin, ether, carbon disulphide, acetone or linseed oil. The lower the melt flow index of a low density polythene the better its chemical and solvent resistance. There is also associated with a lower melt flow index, improved mechanical properties. Therefore, it is important that the lowest melt index of low density polythene consistent with ease of fabrication should be used for all chemical plant and similar applications. Polythene by itself is physiologically inert and can be used in the construction of plant for the food processing industry.

The chemical resistance of high density polythene is generally comparable to that of the low density polythene with respect to aqueous solutions of acids, alkalis and solutions of metallic salts. Strong oxidizing agents and chlorosulphonic acid will cause decomposition of high density polythene in exactly the same way as with low density polythenes.²

It is important to appreciate that scale plays an important part in chemical resistance and that massive sections of polythene may not be greatly affected by conditions fatal to thinner sections. For this and similar reasons it is necessary to carry out chemical resistance tests under conditions as realistic as possible if the material is to be correctly assessed for an intended task. The resistance of polythene to a wide range of materials can be conveniently discussed under the following headings:—

Chemical attack, including oxidation and the effect of such materials as the halogens, acids, alkalis, salt solutions and water.

Permeability to gases, liquids and sulphur.

Absorption. Many liquids, including oils, are absorbed by polythene with resultant reduction in mechanical properties.

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Environmental cracking. This phenomenon is associated with a compressive stress system, and liquid or vapour contact.

CHEMICAL ATTACK

Oxidation

It has been known for some time (see Chapter 6) that serious oxidation of natural polythene takes place in a relatively short time at temperatures in excess of 120°C .³ This results in a rapid rise in power factor, increase in melt viscosity and eventual extensive discolouration. At temperatures just below the melting point in air, the power factor and brittle temperature increase after a few hours, while at 93°C in water exposed to the atmosphere these changes are even more rapid. A disc of low density polythene 0.030 in. thick with an initial brittle point of -50°C was brittle at room temperature after 800 hours in water at 93°C . There are many factors which are important in considering the atmospheric oxidation of any polythene :—

- (a) Temperature.
- (b) Thickness of specimen.
- (c) Presence of pigments.
- (d) Presence of anti-oxidants.

(a) *Effect of temperature.* The increase in power factor with time of exposure of a standard sample of low density polythene in air and in aerated water is shown graphically in Fig. 10.1.

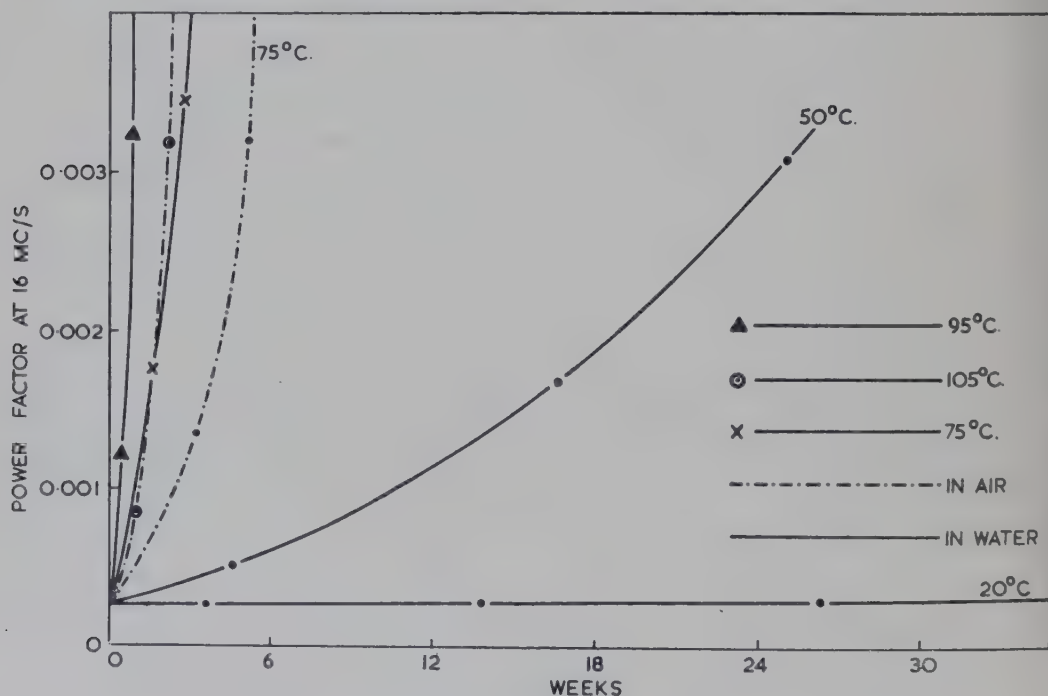


Fig. 10.1. Power factor rise in air and aerated water at various temperatures

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It has been reported that high density polythene coated wire has shown thermal cracking after several hours at elevated temperatures.⁴ Thus it seems that long term exposure of high density polythene to oxygen is no more possible than for low density polythenes even at relatively low temperatures of the order of 80°C. This factor may limit the continuous high temperature performance but will not prevent moulded forms of the new polymers from being sterilized at 110°C (230°F) for 15 minutes.

(b) *The effect of specimen thickness.* This has been discussed by Biggs⁵ who has shown that at thicknesses greater than 5 mm the rate of oxidation is influenced by the rate of diffusion of oxygen into the specimen. Fig.

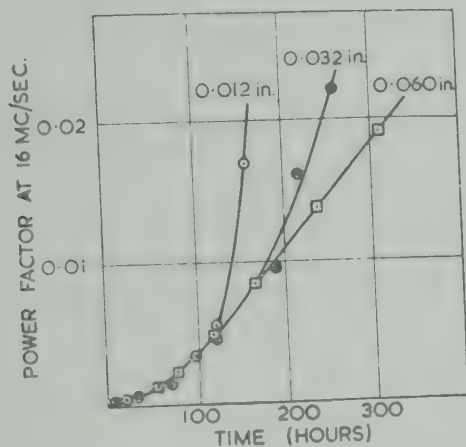


Fig. 10.2. Effect of film thickness on oxidation rate at 105°C

10.2 shows the power factor changes for films of unstabilized polythene of various thicknesses in air at 105°C. The thicker specimens start to oxidize only after an induction period, which is deducted from the total exposure time before plotting in order to facilitate a comparison of the rates of oxidation. It is obvious from these curves that, although in the earlier stages of oxidation the rates of oxidation are substantially the same, in the later stages the rate of oxidation decreases as the film thickness increases. Because the extent of oxidation will be different at various depths below the surface of thick specimens, the overall value of power factor is not necessarily a quantitative measure of the true extent of oxidation. Owing to the laminar effect, $\tan \delta$ will be less (Fig. 6.8) than that for a homogeneous dielectric containing the same number of dipoles. The effect of sample thickness in lowering the overall rate of oxidation is considerable, but at temperatures above 75°C oxidation is still significant in terms of an expected service life of 20 years or more.

(c) *Effect of pigments.* Biggs⁶ has included in the factors which might accelerate the oxidation of low density polythene, the presence of materials such as peroxide and metallic ions of copper, cobalt and manganese. Fig. 10.3 shows the effect of some familiar pigments on the oxidation of low density polythene at 105°C. Cobalt blue is a particularly active catalyst for the oxidation of polythene and should be avoided in all

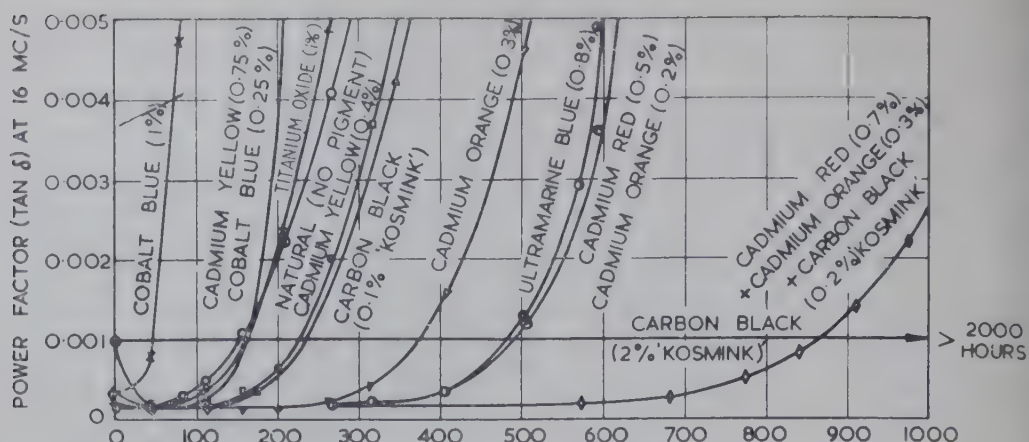


Fig. 10.3. Oxidation of pigmented polythene compositions in air at 105°C

pigment formulations. The curve for carbon black underlines the good anti-oxidant properties of this pigment as previously observed by Wallder and reported by Briggs.⁵ (See Chapter 12).

(d) *Effect of anti-oxidant.* In recent years the increase in the range and type of polythene available and the more exacting performance demanded has increased the need for highly efficient anti-oxidants. Fortunately anti-oxidants for rubber are, in general, effective in polythene and this has greatly increased the range of commercially available anti-oxidants of possible value in polythene. The results which can be obtained by using different anti-oxidants are discussed in Chapter 6. The curves (Fig. 6.7) are characteristic of the autocatalytic nature of the reaction; the efficiency of anti-oxidants is proportional to the length of the induction period. Though there is a slight initial rise in power factor due to the water absorption, oxidation soon becomes the dominant cause of increase and when the anti-oxidant is exhausted or leached out by the water, the rise in power factor is rapid.

U.V. light can cause catalytic oxidation of polythene in air. For this reason, the unprotected material is not recommended for uses where it will be exposed to outdoor weathering: failure by cracking, especially in the case of stressed specimens can occur. This form of attack can be restricted by the addition of 2% carbon black (channel type) having an average particle size of $0.010\text{--}0.020\mu$.¹⁶ Tests have shown that provided the carbon black is evenly dispersed there is little or no deterioration of low density polythene over many years of outdoor exposure. Plates 10.1 and 10.2 illustrate the different types of dispersion of carbon black which can occur.¹⁴ It should be remembered that exposure of black polythene to sunlight can cause very high surface temperatures, so that a thermal anti-oxidant must be used with the carbon black. (See Chapter 6).

Halogens

Liquid and gaseous chlorine both attack polythene. Little quantitative information is, however, available and the only data⁷ are for $\frac{1}{8}$ in. thick

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Table 10.1—EFFECT OF CHLORINE ON POLYTHENE (6 MONTHS' EXPOSURE TO CHLORINE AT 35°C, SAMPLES $\frac{1}{8}$ IN. POLYTHENE SHEET)

	Tensile strength	Elongation %
As received	1,500 lb/sq. in.	500
After exposure	1,000 lb/sq. in.	very low

low density polythene sheet after 6 months' exposure to chlorine at 35°C. Considerable swelling was observed along with the changes in properties shown in Table 10.1.

In spite of this embrittling effect of chlorine, low density polythene instrument tubing has been used for conveying chlorine gas and is widely used in water treatment plant. Samples of tube have been examined after 12 months' service carrying dry chlorine at 10 lb/sq. in. with the following results:—

1. Slight blistering and considerable embrittlement of the bore had occurred as is shown by bend tests with the bore in tension (Plate 10.3).
2. Tensile tests on the full section of the tube were similar to those on new tube.

Table 10.2—EFFECT OF CHLORINE ON TENSILE PROPERTIES

Type of sample	Nominal tensile	% Elongation
New tube	1390 lb/sq. in.	250
After 12 months service	1360 lb/sq. in.	37

Bursting tests on short lengths of new and attacked tube (Table 10.3) showed little difference in bursting pressure although the mode of failure was different (Plate 10.4).

Table 10.3—EFFECT OF CHLORINE ON BURSTING STRENGTH OF POLYTHENE TUBE

	Bursting pressure lb/sq. in.
New tube	1400
Tube after service	1500

While dry chlorine gas does lead to embrittlement of low density polythene the material will give reasonable service, provided that the cross-section is adequate. It must be realized that embrittlement does take place and that it cannot be detected by visual examination. Dilute solutions of chlorine and the various bleaches have little or no effect on low density polythene. Fluorine has a similar effect to chlorine while bromine and iodine are absorbed by and diffused through polythene

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Table 10.4—EFFECT OF SULPHURIC ACID (95%) AT 50°C ON POLYTHENE OF MELT FLOW INDEX 20

Sample size	Percentage increase in weight			
	130 days	160 days	195 days	230 days
2.4 in. × 1.5 in. × 0.17 in.	0.11	0.60	1.22	1.52
1.6 in. × 1.0 in. × 0.086 in.	0.41	1.00	2.05	2.04

with consequent degradation of mechanical properties. It has been shown⁸, however, that such compounds as boron trifluoride have little effect on polythene.

Acids, alkalis and aqueous salts

Low density polythene is little affected by all but those acids which have an oxidizing effect at high concentrations. It is unaffected by all concentrations of hydrofluoric acid. Sulphuric acid does not attack polythene even when the acid concentration is as high as 80% and although at 98% some darkening of both the acid and the polythene occurs, polythene vessels are used to carry acid at this concentration.

Nitric acid, which is a more powerful oxidizing agent, causes blistering of low density polythene when the acid concentration is greater than 25%. Table 10.5 shows the general effect of nitric acid on low density polythene and it will be seen that the rate of attack is closely related to the operating temperature.

The resistance of low density polythene to oxidizing acids generally decreases with increase in temperature; lower limits of concentrations have to be accepted at higher operating temperatures. Hydrochloric acid at any concentration does not affect polythene. The majority of organic acids have no effect other than in the special circumstances to be mentioned later (under Environmental Cracking).

Polythene is highly resistant to alkalis and remains unaffected by all concentrations of sodium and potassium hydroxides even at 60°C although

Table 10.5—EFFECT OF NITRIC ACID ON POLYTHENE OF MELT INDEX 2

Acid concentration	3 months at 20°C		1 week at 40°C		1 week at 60°C	
	Weight increase	Decrease in elongation at break	Weight increase	Decrease in elongation at break	Weight increase	Decrease in elongation at break
50%	0.2%	Nil	0.4%	18%	4.5%	70%
80%	1.9%	40%	9.7%	100%	17.1%	100%
95%	6.9%	75%	14.9%	100%	23.7%	100%

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environmental cracking may occur under certain special circumstances. Aqueous solutions of inorganic salts do not affect polythene up to about 60°C.

Water

Polythene, of both high and low density, is very resistant to water and water vapour and is one of the best moisture barriers available. It is able to maintain flexibility and moisture vapour resistance even when flexed repeatedly at low temperatures. The permeability of low density polythene film to water vapour is so low that only 18 gms of water vapour will pass through a square metre of 0.001 in. film in 24 hours at 38°C at 90% relative humidity. The permeability of low density polythene to

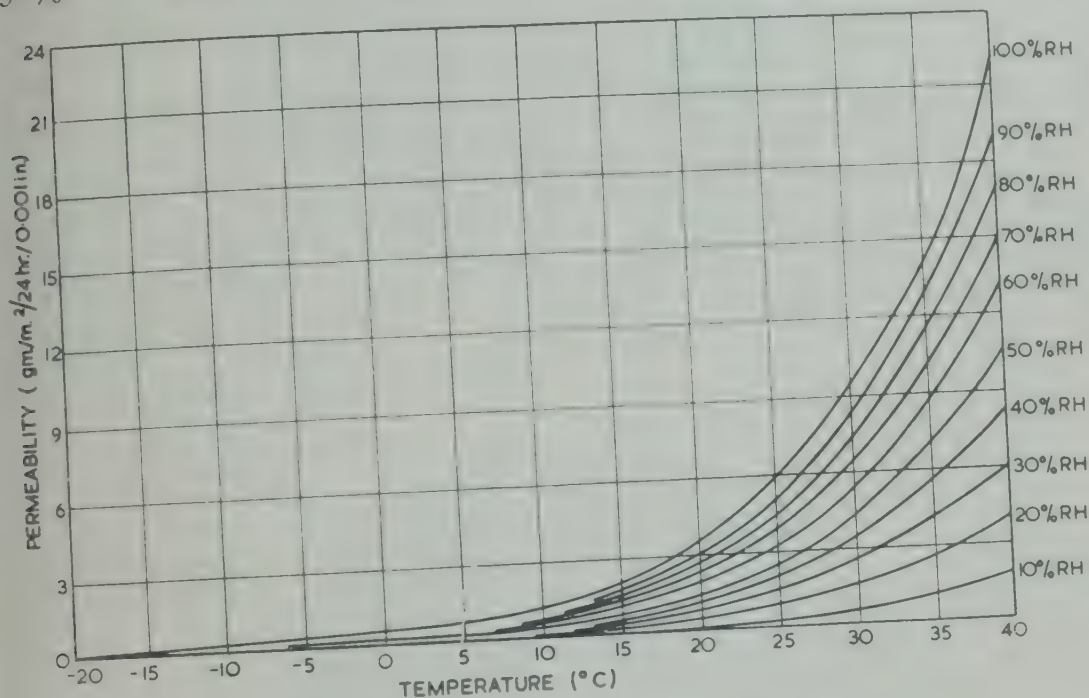


Fig. 10.4. Water vapour permeability of polythene film

water vapour over a wide range of temperatures and relative humidities is shown in Fig. 10.4.

Polythene has one of the lowest water absorption values of any commercial plastics. The gain in weight of low density polythene immersed in water amounts to 0.15% by weight in 1 year at 20°C. (Fig. 10.5).

PERMEABILITY

The permeation of gases through thin films of polythene has been studied fairly extensively, but data for thicker sections have to be deduced by extrapolation rather than by direct measurement. Polythene is an excellent barrier to most liquids and some work has been done recently on the shelf life of a number of liquids in polythene bottles.⁹ There are

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some liquids such as ethers, hydrocarbons and chlorinated hydrocarbons which permeate through polythene film fairly rapidly. In addition some essential oils diffuse through it and finally evaporate from the outer surface. Table 10.6 gives typical examples of the values obtained.

Table 10.6—PERMEABILITY OF SOME ETHERS, HYDROCARBON AND ESSENTIAL OILS
(MEASURED AT 20°C IN GMS/SQ. CM/24 HRS/0.001 IN.)

Liquid	Permeability
Dibutyl ether	3100
Diethyl ether	6355
Ethyl bromide	10540
Chloroform	11160
Lemon oil	441
Orange oil	435
Grapefruit oil	519

Polythene film is slowly permeated by gases and the rate varies with the type of gas under consideration. In some packaging applications it is essential to retain the gases in the package while in others the gases must be removed fairly quickly otherwise the product will deteriorate.

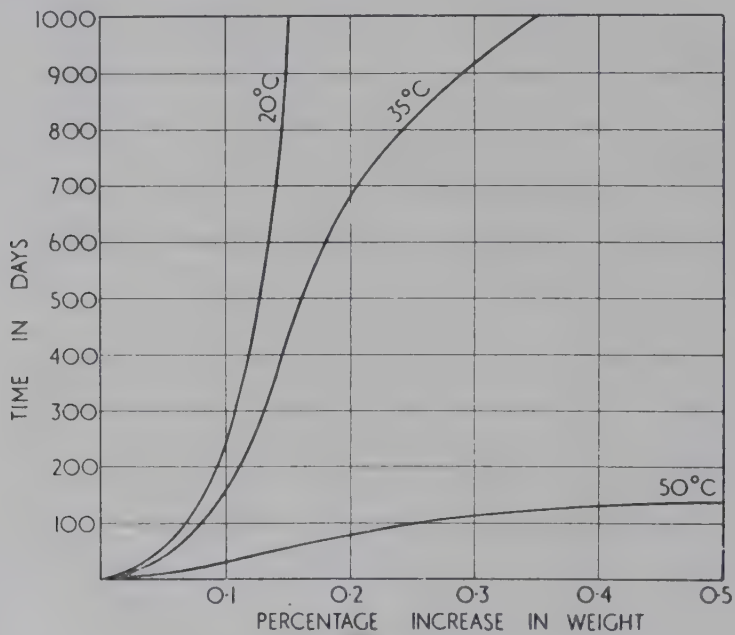


Fig. 10.5. Water absorption of polythene (melt flow index 20)

Thus, where a correct gas permeability is important, it is essential that polythene is tested under the proposed operation conditions. The figures in Table 10.7 are typical of the permeability rate of a number of gases through a 1 mm thick film of low density polythene with a partial pressure

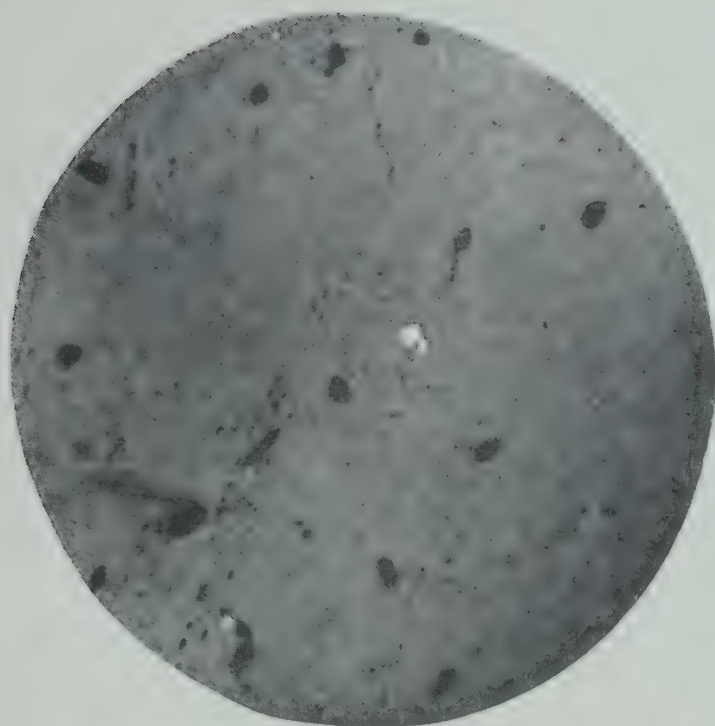


Plate 10.1. Photomicrographs of good carbon black dispersion

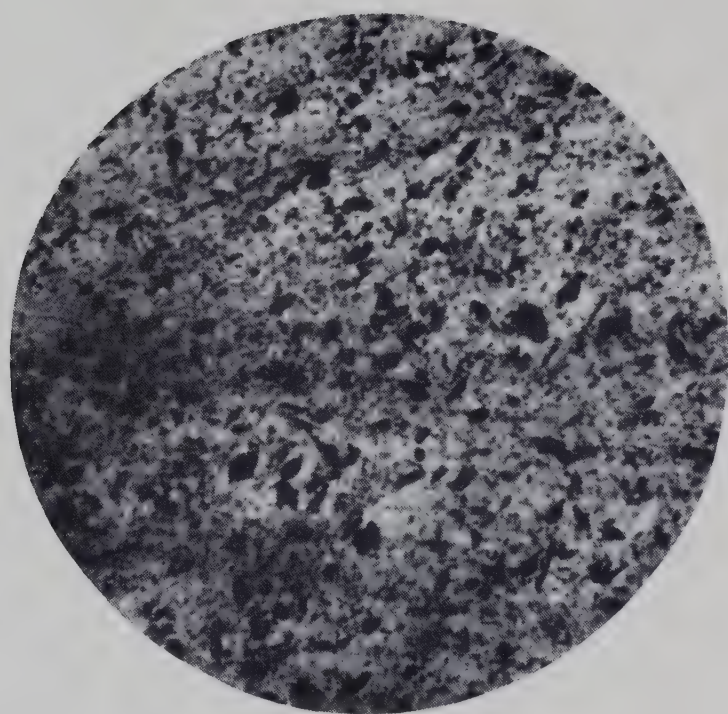
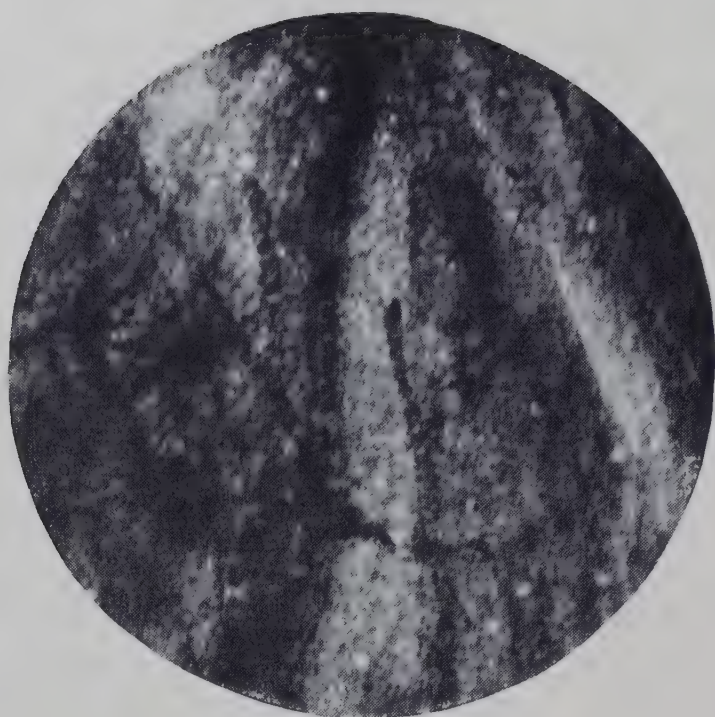


Plate 10.2. Photomicrographs of bad carbon black dispersion



Plate 10.3. Bend test showing embrittlement effect of chlorine

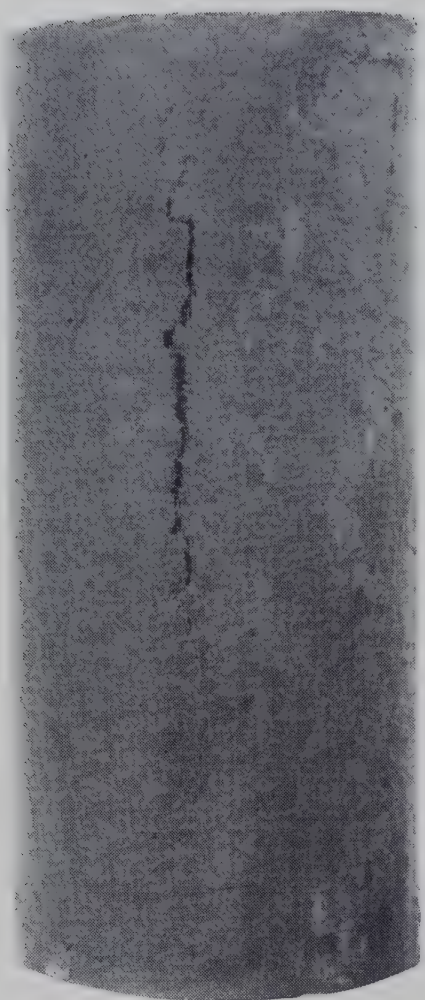


Plate 10.4. Difference in ductility of polythene resulting from exposure to chlorine

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Table 10.7—PERMEABILITY RATE OF GASES THROUGH LOW DENSITY POLYTHENE FILM, 1 MM THICK, AT 20°C (PERMEABILITY IN CC/SQ. M/24 HRS/MM.)

Gas	Permeability
Carbon dioxide	8.64
Hydrogen	6.20
Methane	6.05
Oxygen	2.76
Ethane	0.99
Nitrogen	0.95

differential of 1 cm of mercury across the film and at a temperature of 20°C.

Certain acid vapours such as hydrochloric and nitric acid permeate quite rapidly through polythene film and it is not recommended for use where such vapours are evolved. Despite these restrictions, polythene compares favourably with glass in its inertness to a wide range of chemicals.⁹

Sulphur is slowly absorbed by low density polythene of all melt flow indexes. While this absorption may adversely affect the electrical properties of polythene in particular its power factor, there is no marked deterioration in the mechanical properties. Certain organic sulphur-containing compounds have a similar but greater effect. The diffusion of such compounds can cause tarnishing of copper conductors.

It has been reported that the resistance to penetration of gases and liquids is greater in the case of high density polythene than with low density polythene.¹⁰ This improvement in permeability rate of such gases as hydrogen, carbon dioxide and oxygen is of the order of 50–80% depending upon the density of the polymer, and in the case of alcohols, essential oils and chlorinated solvents the improvement is said to be of the same order.² Typical figures quoted for gas permeability are given in Table 10.8.

ABSORPTION

At temperatures above 60°C low density polythene is appreciably soluble in liquids which are good solvents for polythene. They are readily

Table 10.8—COMPARISON OF GAS PERMEATION THROUGH POLYTHENE (PERMEABILITY IN CC/SEC/CM²/CM/CM Hg PARTIAL PRESSURE × 10¹¹)

	Low density polythene (0.92)	High density polythene (0.96)
Hydrogen	0.9	0.21
Oxygen	0.3	0.08
Carbon dioxide	1.45	0.23
Methane	0.7	0.09

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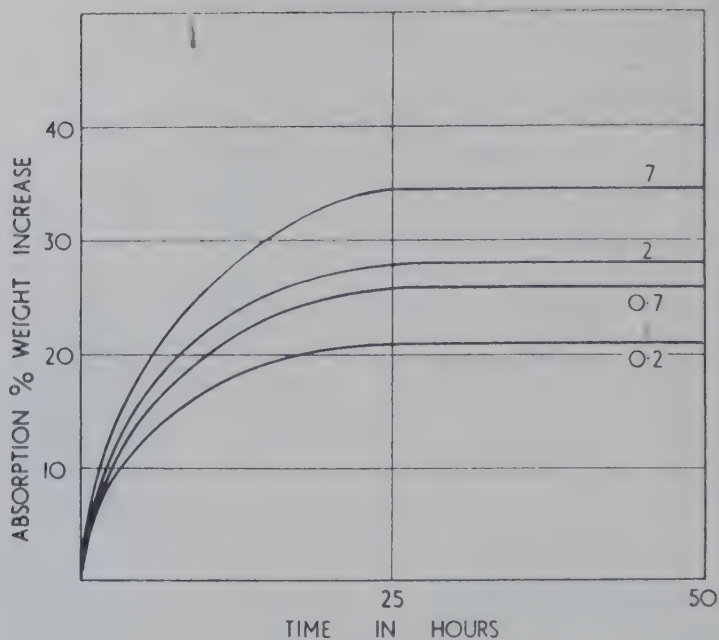


Fig. 10.6. Absorption of high octane aviation spirit by polythene of different melt flow indexes. Specimens were $1\frac{1}{2}$ in. \times $\frac{1}{2}$ in. \times $1/16$ in. and absorption was measured at 50°C

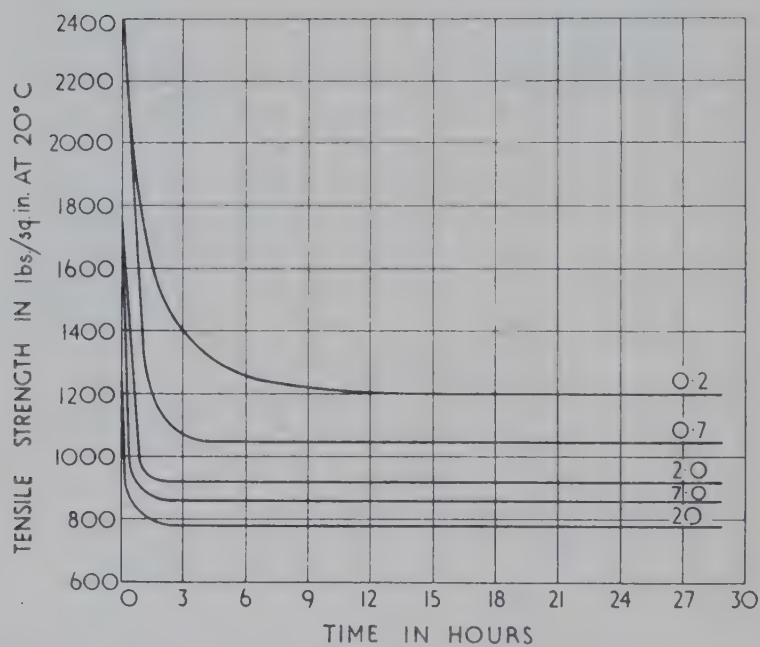


Fig. 10.7. Absorption effect of aviation spirit on tensile strength at break of polythenes of different melt flow indexes. Specimens were $1\frac{1}{2}$ in. \times $\frac{1}{2}$ in. \times $1/16$ in.

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absorbed by polythene with consequent swelling and decrease in mechanical properties. The amount of any liquid which is absorbed by polythene increases with temperature but decreases as the melt flow index of the polymer falls.

In containers, liquids which are solvents at high temperatures are not only absorbed by the low density polythene, but also permeate through it. Volatile liquids evaporate from the outer surface, while liquids of low volatility appear on the outer surface. The rate of diffusion depends upon several factors, including wall thickness, the temperature and difference in vapour pressure within and without the container.

The difference in diffusion rates between compounds of similar structure may be quite considerable and, in a mixture, may result in changes of composition with time. In general, the greater the absorption the faster the rate of permeation. The range is very wide, from carbon tetrachloride and benzene, which permeate rapidly, to ethyl alcohol and water, whose permeation rates are so small as to be negligible for practical purposes. The lower the melt flow index of the polythene used, the lower is the maximum absorption as Table 10.9 shows.

Table 10.9—MAXIMUM ABSORPTION^a AND MELT FLOW INDEX OF POLYMER

Liquid	Weight increase (%)			Volume increase (%)		
	melt flow index			melt flow index		
	2	20	200	2	20	200
Carbon tetrachloride	38	44	45	20.5	22	27
Benzene	12	13.5	14	12	14	14.5
Methanol	0.1	0.1	0.2	Negligible		

^a This level is reached in approximately one week at 20°C.

Absorption results in a degradation of mechanical properties; the absorbed molecule enters the polythene structure and so reduces the inter-molecular forces and consequently the tensile strength of the material (Figs. 10.6 and 10.7). The maximum reduction in strength is reached when maximum absorption has been achieved. Thus, with aviation spirit at 50°C the tensile strength of low density polythene falls by approximately 45% to a constant value of 950 lb/sq. in. at an absorption level of 28%. In the case of injection moulded components, absorption can result in a general reduction in mechanical properties but in this particular case any physical weaknesses due to the injection process become magnified. Thus weld lines and areas become regions of extreme weakness at even low absorption. In some cases the laminar structure of injection moulded sections becomes apparent and, in the extreme, separation of a surface layer is observed.

All oils attack low density polythene but the greatest effect is caused by mineral oils which will dissolve it at elevated temperatures. At lower

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Table 10.10—ABSORPTION OF OILS BY POLYTHENE (MELT FLOW INDEX 2) AT 50°C

Oil	% Weight increase
Transformer oil	15
Linseed oil	0.1
Ground nut oil	1.0
Olive oil	0.25
Tung oil	1.2
Tallow	1.7
Whale oil	2.4
Sardine oil	1.5

temperatures, absorption of oils causes swelling and discolouration; with low density polythenes of high melt flow index disintegration of the polymer can take place. Vegetable and animal oils do not produce such a drastic effect as mineral oils.

High density polythenes have initially higher tensile strengths than low density polythenes and the loss of strength due to absorption still results in a product mechanically stronger than low density polythene. The results in Table 10.11 on the effect of the absorption of aviation spirit on two polymers illustrate this fact.

Similarly it has been reported that low density polythene is dissolved in benzene at its boiling point while high density polythene is only swollen.

The resistance of the new high density polymers to environmental cracking is good. It must be realized, however, that most of the high density polythenes have melt flow indexes of the order of 0.2–0.7 as compared with 2 for low density polythenes. Thus if polymers of equal melt flow indexes are examined then the new polymers have no greater resistance to environmental cracking than conventional polythenes.

ENVIRONMENTAL CRACKING

When polythene is bi- or polyaxially stressed in contact with certain liquids and vapours it tends to rupture under conditions which it might withstand indefinitely if these materials were not present*. It has been known for some time¹¹ that if moulded specimens of some grades of low

Table 10.11—ABSORPTION OF AVIATION SPIRIT BY POLYTHENE

Density	Maximum absorption %	Ultimate tensile strength (lb/sq. in.)		Elongation %	
		Original	After absorption	Original	After absorption
0.95	6.8	3570	3070	320	200
0.92	20.7	2400	1310	600	420

* See Chapters 9 and 11

density polythene with melt index greater than 2 are stressed in contact with polar organic solvents like methanol and acetone, mechanical failure occurs due to cracking. The amount of reagent absorbed at equilibrium is usually very small and the phenomenon sometimes takes a considerable interval to appear, but with very active reagents, failure can occur very quickly. Failure can, of course, occur with substances which are solvents for polythene, but these are absorbed to a considerable extent resulting in the polythene swelling and softening. Recent reports¹² indicate that a wider group of materials can cause this type of failure associated with polar solvents than had hitherto been appreciated. This phenomenon has been described as environmental stress cracking, environmental cracking, or solvent embrittlement. It is similar to the stress crazing of other polymeric materials, e.g. polystyrene and polymethyl methacrylate and to the stress cracking of certain metals. Failure is usually observed in the form of sharp conchoidal fractures.

The incidence and extent of cracking is determined by four factors:

- (a) the type of polythene;
- (b) the activity of the environment;
- (c) the magnitude of the applied stress;
- (d) the magnitude of residual strain.

(a) *Type of polythene*

The resistance to environmental cracking is a function of molecular weight and structure and this has been discussed by Richards.¹³ Materials with a high molecular weight (low melt flow index) shows a greater resistance to cracking than materials of low molecular weight (high melt flow index). Thus melt index 20 is rapidly cracked by a wide variety of active environments, whereas melt index 0.2 remains unaffected under the same conditions. The addition of polyisobutylene or butyl rubber greatly improves the resistance of some polythenes to cracking.* Unless grades or mixtures of polythenes are used which are immune to this cracking phenomena it is clearly most important to avoid undue stress in components that are likely to encounter an organic environment.

(b) *Effect of environment*

Materials widely differ in their power to produce this cracking phenomenon and the more pronounced the polar nature of the reagent the greater is its activity. Active environments include: alcohols, aldehydes and ketones, organic acids, esters, surface active agents (detergents) essential oils, fixed oils, animal oils and silicone fluids.

(c) *Magnitude of the applied stress*

Unstressed polythene does not crack in an active environment. It has been shown that if the stress is effectively uniaxial and if the surface of the specimen is free from flaws it does not usually result in failure;

* Cf. Chapters 9 and 25.

similarly there appears to be a critical stress below which a polythene section does not crack, even when the stress system is multi-axial. For polythenes of melt index 2 and lower this is usually very much higher than the material would be expected to withstand during normal use.

(d) *Magnitude of residual strain*

The degree of frozen-in molecular orientation is an important factor in determining the susceptibility of a fabricated polythene article to environmental cracking. Thus an injection moulded bottle (from material of melt flow index) 20 cracks after only one flexure in acetone, whereas a blown bottle from the same grade, (i.e. strain free) shows no sign of failure after 1,500 similar flexes. In the injection moulding process, due to the high shearing forces operating during the filling of the mould cavity, a high degree of molecular orientation is introduced. In all injection mouldings, the area around the sprue is particularly vulnerable and care is necessary on removing the sprue. The blow moulding process is, by its very nature, one where the minimum amount of frozen-in molecular orientation is produced, and the factors which determine the environmental behaviour of such a container are only (a), (b) and (c) above. Failure, can of course, occur with substances which are true solvents for polythene but these are absorbed strongly causing the polythene to swell and soften. Solvents for low density polythene which act in this way include petroleum products, aromatic hydrocarbons and chlorinated hydrocarbons. The extent of absorption depends on molecular weight and crystallinity. The higher the molecular weight of the polythene the less is the absorption, and the greater the crystallinity of the polythene the less is the absorption.

TESTING FOR ENVIRONMENTAL CRACKING

A laboratory test, of necessity arbitrary and qualitative in nature, was developed for the purpose of defining the type and range of materials which could cause cracking. The results are of interest not only to the cable industry, but in the packaging and chemical plant fields where active environments may be encountered. They suggest whether or not polythene is a suitable material for use in the conditions to be imposed and help in the selection of the right grade of polythene. It should be emphasized that the results are those of laboratory tests and there is not full correlation between these and the field experience. The laboratory test is a stringent and searching one and is of real assistance in giving some forecast of what may happen in service.

The laboratory test used was that developed by the Bell Telephone laboratory¹² and is referred to as the B.T.L. test. The principle is to immerse a standard specimen bent by a predetermined amount and on the surface of which is a scratch to cause stress concentration, in the selected reagent. It is usual to classify the particular grade of polythene as immune to cracking if it withstands the above test in a specified reagent for 300 hours. (See chapters 9 and 11.)

Table 10.12—ENVIRONMENTAL CRACKING OF LOW DENSITY POLYTHIENES OF A WIDE RANGE OF MELT FLOW INDEX

Reagent	Melt flow index				
	0.2	0.7	2	7	20
Acetone	N.C.	N.C.	22	X	X
Aniline	N.C.	N.C.	48	0.5	0.5
Butyl alcohol	N.C.	N.C.	96	X	X
Cresylic acid	N.C.	N.C.	300	X	X
Ethyl alcohol	N.C.	N.C.	18	X	X
"Lissapol" N	N.C.	12	3.25	1.25	0.25
Milk	N.C.	N.C.	N.C.	120	9
Oil of bergamot	N.C.	N.C.	72	X	X
Oil of turpentine	N.C.	43	8	0.5	0.5
Olive oil	N.C.	N.C.	N.C.	1	0.25
Tung oil	N.C.	N.C.	N.C.	72	0.25
Silicone fluid B 511	N.C.	20	5	0.5	X

All times are measured in hours.

N.C. = no cracking observed in 300 hours.

X = all samples cracked immediately

THE EFFECT OF ORGANIC LIQUIDS

It is not possible to generalize regarding the use of polythene with organic liquids, since function, size and other variables can all influence the problem. For instance, small polythene tubes can be used for carrying hydrocarbon fuel, since dimensional changes are unimportant and because the level of strain due to flexure are well below the critical limits that might induce environmental cracking. Similarly effluent drains based on large diameter low density polythene pipe are operating quite satisfactorily with liquids which contain organic fluids: this has been achieved by ensuring strain free installations. In contrast, extraction ducts have failed in the presence of wetting agents carried over in otherwise harmless sprays. Such failures are often due to bad design and unsound installation which combine to produce some critical limits of multi-axial strain. Thus, in chemical plant it is essential to use the correct grade of polythene, and to ensure a low level of strain.

Table 10.12 gives the results obtained with a selected range of environments on low density polythene of a wide range of melt indexes.

From the results in Table 10.12 it will be seen that a polythene having a melt flow index of less than 0.7 is not embrittled even by the most active of the environments used in the present series of tests.

Table 10.13 should serve as a guide to the probable performance of low density polythene under a wide variety of conditions. The information in this table has been obtained mainly from laboratory tests and in consequence a potential user should satisfy himself that polythene will prove serviceable under actual working conditions. This recommendation is particularly important where mixtures of chemicals are being handled.

For references see p. 220

Table 10.13—THE CHEMICAL RESISTANCE OF POLYTHENE

The following key has been used in these tables:

- ▲ indicates SATISFACTORY
 □ indicates SOME ATTACK OR ABSORPTION
 (may be considered where alternative materials are unsatisfactory)
 ○ indicates UNSATISFACTORY
 a indicates POSSIBILITY OF ABSORPTION WITH
 LOSS OF MECHANICAL PROPERTIES
 e indicates POSSIBILITY OF "ENVIRONMENTAL CRACKING"

The ratings quoted are for a polythene of melt index 2 and density 0.92

Chemical	Concentration	Temperature		Absorption or environmental cracking hazard	Chemical	Concentration	Temperature		Absorption or environmental cracking hazard
		20°C	60°C				20°C	60°C	
Acetaldehyde	100%	□	○	e	Alcohol, furfuryl		○		e
Acetic acid	10% 60% Glacial	▲ ▲ □	▲ ▲ ○		Alcohol, methyl	6% 100%	▲ □		
Acetone	100%	○	○	e	Alum		▲	▲	
Alcohol, amyl		▲		e	Aluminium chloride		▲	▲	
Alcohol, butyl		▲		e	Aluminium fluoride		▲	▲	
Alcohol, cetyl		▲		e	Aluminium hydroxide		▲	▲	
Alcohol, ethyl	40% w/water 100%	▲	○	e	Aluminium sulphate		▲	▲	

Table 10.13 (contd.)—THE CHEMICAL RESISTANCE OF POLYTHENE

Chemical	Concentration	Temperature		Absorption or environmental cracking hazard	Chemical	Concentration	Temperature		Absorption or environmental cracking hazard
		20°C	60°C				20°C	60°C	
Ammonia	0.88 s.g. soln. dry gas	▲	▲		Ammonium thiocyanate		▲	▲	
Ammonium bicarbonate		▲	▲		Amyl acetate		○		e
Ammonium carbonate		▲	▲		Aniline		○		e
Ammonium chloride		▲	▲		Aniline hydrochloride		○		
Ammonium hydro-sulphide		▲	▲		Aniline sulphate		○		
Ammonium hydroxide		▲	▲		Animal oils		□	○	e
Ammonium meta-phosphate		▲	▲		Antimony chloride		▲	▲	
Ammonium nitrate		▲	▲		Antimony trichloride		▲	▲	
Ammonium persulphate		▲	▲		Arsenic acid	Conc.	▲	▲	
Ammonium phosphate		▲	▲		"Arcton" 6		□		e
Ammonium sulphate		▲	▲		Barium carbonate		▲	▲	
Ammonium sulphide		▲	▲		Barium chloride		▲	▲	
		▲	▲		Barium hydroxide		▲	▲	

Table 10.13 (contd.)—THE CHEMICAL RESISTANCE OF POLYTHENE

Chemical	Concentration	Temperature		Absorption or environmental cracking hazard	Chemical	Concentration	Temperature		Absorption or environmental cracking hazard
		20°C	60°C				20°C	60°C	
Barium sulphate		▲	▲		Calcium bisulphite		▲	▲	
Barium sulphide		▲	▲		Calcium carbonate		▲	▲	
Beer		▲	▲		Calcium chlorate		▲	▲	
Benzaldehyde	100%	○		e	Calcium chloride		▲	▲	
Benzene		○		a	Calcium hydroxide		▲	▲	
Benzene-sulphonic acid		○			Calcium hypochlorite		▲		
Benzyl alcohol		○			Calcium nitrate		▲		
Bismuth carbonate		▲	▲		Calcium phosphate		▲		
Borax		▲	▲		Calcium sulphate		▲		
Boric acid		▲	▲		Camphor oil		○		e
Boron trifluoride		▲			Carbon dioxide		▲		
Brine		▲	▲		Carbon disulphide		○		
Bromine	100% dry gas	○			Carbon monoxide		▲		

Table 10.13 (contd.)—TIE CHEMICAL RESISTANCE OF POLYTHENE

Chemical		Concentration	Temperature		Absorption or environmental cracking hazard
			20°C	60°C	
Carbon tetrachloride			○		a
Castor oil			○		e
Chloral hydrate			○		
Chlorine	100% dry gas liquid		□ ○	○	
Chlorine water	2% sat. soln.		▲ ▲	▲ □	
Chloroform			○		e
Chlorosulphonic acid			○	○	
Chrome alum			▲	▲	
Chromic acid	Plating soln.		▲	▲	
Cider			▲		
Citric acid			▲	▲	
Copper chloride			▲	▲	

Table 10.13 (*contd.*)—THE CHEMICAL RESISTANCE OF POLYTHENE

Chemical	Concentration	Temperature		Absorption or environmental cracking hazard	Chemical	Concentration	Temperature		Absorption or environmental cracking hazard
		20°C	60°C				20°C	60°C	
Developers, photographic		▲	▲	e	Ferric sulphate		▲		
Dextrose		▲	▲		Ferrous ammonium citrate		▲	▲	
Dibutyl phthalate		□	○	e	Ferrous sulphate		▲	▲	
Diethyl ether		○	○	e	Fixing solution, photographic		▲	▲	
Diethylene glycol		▲			Fluorine		□	○	
Diocetyl phthalate		□	○	e	Fluosilicic acid		▲		
Disodium phosphate		▲			Formaldehyde	40% w/water	▲	▲	
Emulsifiers	All conc.	▲			Formic acid	3% 10% 25% 50% 100%	▲ ▲ ▲ ▲ ▲	▲ ▲ ▲ ▲ ▲	
Emulsions, photographic		▲			Fruit pulp		▲		
Ether		○		e	Furfuryl alcohol		○		e
Ethyl acetate		□	○		Glucose		▲		
Ethylene dichloride		○		e					
Ferric chloride		▲							

Table 10.13 (contd.)—THE CHEMICAL RESISTANCE OF POLYTHENE

Chemical	Concentration	Temperature		Absorption or environmental cracking hazard	Chemical	Concentration	Temperature		Absorption or environmental cracking hazard
		20°C	60°C				20°C	60°C	
Glycerine		▲	▲		Hypochlorous acid		□	○	
Grape sugar		▲	▲		Lactic acid	10% 100%	▲ ▲	▲ ▲	
Hydrobromic acid	50% 100%	▲ ▲	▲ ▲		Lead acetate		▲		
Hydrochloric acid	10% 22% Conc.	▲ ▲ ▲	▲ ▲ ▲		Lead arsenate		▲		
					Lead tetra-ethyl		▲		
Hydrofluoric acid	4% 40% 60% Conc.	▲ ▲ ▲ ▲	▲ ▲ ▲ □		Linseed oil		□	○	e
					Magnesium carbonate		▲	▲	
Hydrogen		▲	▲		Magnesium chloride		▲	▲	
					Magnesium hydroxide		▲	▲	
Hydrogen peroxide	3% (10 vols) 12% (40 vols) 30% (100 vols) 90% and above	▲ ▲ ▲ ▲			Magnesium nitrate		▲	▲	
					Magnesium sulphate		▲	▲	
Hydrogen sulphide		▲			Maleic acid	25% 50% Conc.	▲ ▲ ▲	▲ ▲ ▲	
Hydroquinone		▲							

Table 10.13 (contd.)—THE CHEMICAL RESISTANCE OF POLYTHENE

Chemical	Concentration	Temperature		Absorption or cracking hazard	Chemical	Concentration	Temperature		Absorption or cracking hazard
		20°C	60°C				20°C	60°C	
Manganese sulphate		▲	▲		Nickel nitrate		▲	▲	
Mercuric chloride		▲	▲		Nickel sulphate		▲	▲	
Mercuric cyanide		▲	▲		Nitric acid	5% 10% 25% 50% 70% 95%	▲	▲	
Mercury		▲					▲	▲	
Metallic soaps		▲					▲	▲	
Methyl acetate		○	○	e			□	○	
Methyl bromide		□	○				▲	▲	
Methyl chloride		○	○				▲		
Methyl ethyl ketone		□	○	e	Nitrobenzene		□	○	e
Milk		▲			Oxalic acid		▲	▲	
Mineral oils		□	○	a	Oxygen		▲		
Monochlorobenzene		○	○		Paraffin		□	○	a
Nickel chloride		▲	▲		Petrol		○	○	a
					Petroleum ether		○	○	a
					Phenol		○		e
					Phosphoric acid	25%	▲	▲	

Table 10.13 (contd.)—THE CHEMICAL RESISTANCE OF POLYETHYLENE

Chemical	Concentration	Temperature		Absorption or environmental cracking hazard	Chemical	Concentration	Temperature		Absorption or environmental cracking hazard
		20°C	60°C				20°C	60°C	
Phosphoric acid	30% 50% 95%	▲	▲		Potassium borate		▲	▲	
		▲	▲		Potassium bromate		▲	▲	
		□	○		Potassium bromide		▲	▲	
Phosphorus oxychloride		○	○		Potassium carbonate		▲	▲	
Phosphorus pentoxide		▲	▲		Potassium chlorate		▲	▲	
Phosphorus trichloride		▲			Potassium chloride		▲	▲	
Photographic developers		▲		e	Potassium chromate		▲	▲	
Photographic emulsions		▲			Potassium cuprocyanide		▲	▲	
Photographic fixing soln		▲			Potassium cyanide		▲	▲	
Picric acid	1% w/water 10% w/alcohol	▲			Potassium dichromate		▲	▲	
Potassium acid sulphate		▲	▲		Potassium ferricyanide		▲	▲	
Potassium bicarbonate		▲	▲		Potassium ferrocyanide		▲	▲	
Potassium bichromate		▲	▲		Potassium fluoride		▲	▲	
Potassium bisulphite		▲	▲						

Table 10.13 (contd.)—THE CHEMICAL RESISTANCE OF POLYTHENE

Chemical	Concentration	Temperature		Absorption or environmental cracking hazard	Chemical	Concentration	Temperature		Absorption or environmental cracking hazard
		20°C	60°C				20°C	60°C	
Potassium hydroxide	1% 10% Conc.	▲	▲	e	Silver cyanide		▲	▲	
		▲	▲		Silver nitrate		▲	▲	
		▲	▲		Soap solution		▲	▲	
Potassium nitrate		▲	▲		Sodium acetate		▲	▲	
Potassium perborate		▲	▲		Sodium acid sulphate		▲	▲	
Potassium permanganate		▲	▲		Sodium aluminate		▲	▲	
Potassium persulphate		▲	▲		Sodium benzoate		▲	▲	
Potassium phosphate		▲	▲		Sodium bicarbonate		▲	▲	
Potassium sulphate		▲	▲		Sodium bisulphate		▲	▲	
Potassium sulphide		▲	▲		Sodium bisulphite		▲	▲	
Potassium thiosulphate		▲	▲		Sodium borate		▲	▲	
Salicylic acid		▲	▲		Sodium bromide		▲	▲	
Sea water		▲	▲		Sodium carbonate		▲	▲	
Silicone fluids		□		e					

Table 10.13 (contd.)—THE CHEMICAL RESISTANCE OF POLYTHENE

Chemical	Concentration	Temperature		Absorption or environmental cracking hazard
		20°C	60°C	
Sodium chlorate		▲	▲	
Sodium chloride		▲	▲	
Sodium cyanide		▲	▲	
Sodium ferricyanide		▲	▲	
Sodium ferrocyanide		▲	▲	
Sodium fluoride		▲	▲	
Sodium hydroxide	1% 10% 40% Conc.	▲ ▲ ▲ ▲	▲ ▲ ▲ ▲	e
Sodium hypsulphate		▲	▲	
Sodium hypochlorite	15% Cl.	▲	▲	
Sodium metaphosphate		▲	▲	
Sodium nitrate		▲	▲	
Sodium nitrite		▲	▲	
Sodium peroxide		▲	▲	
Sodium phosphate		▲	▲	
Sodium silicate		▲	▲	
Sodium sulphate		▲	▲	
Sodium sulphide	25%	▲	▲	
Sodium sulphite		▲	▲	
Sodium thiosulphate		▲	▲	
Soft soap		▲	▲	e
Stannic chloride		▲	▲	
Stannous chloride		▲	▲	
Starch		▲	▲	

Table 10.13 (contd.)—THE CHEMICAL RESISTANCE OF POLYTHENE

Chemical	Concentration	Temperature		Absorption or environmental cracking hazard	Chemical	Concentration	Temperature		Absorption or environmental cracking hazard
		20°C	60°C				20°C	60°C	
Stearic acid		▲	▲		Tannic acid		▲	▲	
Sucrose		▲	▲		Tanning extracts		▲	▲	
Sulphur	Colloidal	▲			Tartaric acid	10%	▲	▲	
Sulphur dioxide	100% dry 100% moist	▲▲			Toluene		○	○	a
Sulphuric acid	10%	▲	▲		Transformer oil		□	○	a
	20%	▲	▲		Trichlorethylene		○	○	a
	30%	▲	▲		Tricresyl phosphate		○	○	e
	40%	▲	▲		Triethanolamine		□	○	e
	50%	▲	▲		Trisodium phosphate		▲	▲	
	60%	▲	▲		Turpentine		□	○	e
	70%	▲	▲						
	95%	□	○						
	98%	□	○						
	Fuming	○	○						
Surface active agents (Emulsifiers, synthetic detergents and wetting agents)	Normal dilutions	▲	▲	e	Vegetable oils		□	○	e
Tallow					Vinegar		▲	▲	
		▲			Water		▲	▲	

Table 10.13 (contd.)—THE CHEMICAL RESISTANCE OF POLYTHENE

Chemical	Concentration	Temperature		Absorption or environmental cracking hazard	Chemical	Concentration	Temperature		Absorption or environmental cracking hazard
		20°C	60°C				20°C	60°C	
Wetting agents	Normal Dilutions	▲	▲	e	Yeast		▲		
Whey		▲			Zinc chloride		▲	▲	
Wines and spirits		▲			Zinc oxide		▲	▲	
Xylene		○	○	a	Zinc sulphate		▲	▲	

POLYTHENE

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CHAPTER 11

TESTING AND SPECIFICATIONS

S. J. BARKER

THE variety of ethylene polymers which has been produced since the discovery of polythene in 1933 is very wide, ranging from low molecular weight greases and brittle waxes (mol. wt. of the order of 1,000) up to and beyond the toughest high molecular weight resins at present commercially produced (mol. wt. 50-60,000). Even within the narrower molecular weight range which is at present commercially exploited there exists a wide gradation of properties, and quite marked differences, due to variations of molecular structure and distribution, can be observed between two polythenes of the same average molecular weight.

Furthermore, with the introduction recently of new processes for manufacturing polythenes of higher densities, polymers totally different in properties and behaviour from those at present being produced have become available. It is therefore necessary to include, in a specification for a given application, one or more tests to characterize the type of material required. It is these characterization tests which form the main part of this chapter. In addition to specifying the fundamental properties of the material, it is also often necessary to specify its quality, i.e. freedom from gross contamination or degree of oxidation. The third type of test which is often included in specifications concerns analytical methods for the determination of material such as polyisobutylene, carbon black and other substances which are compounded with polythene for certain applications.

The tests which are described in the following pages have been developed over the years since the discovery of polythene, and therefore refer to polythene of conventional density (0.92 gm/cm^3). Some of the tests may be found, as experience becomes wider, to be less suited to the new polymers of higher density, but in the present stage of knowledge results are being quoted on the existing tests. Users of high density polythene will probably be attracted by new properties, such as increased softening temperature and stiffness, for which standard test methods for polythene have yet to be accepted.

High density polythene greatly widens the available range of properties, and makes the problem of providing a unique characterization test far more difficult.

The melt flow index test which has been of some value in characterizing polythene in the past will no longer be of value unless it is accompanied by a figure for the density.

POLYTHENE

PHYSICAL TESTS

In all physical tests on polythene, attention must be paid to the wide variability in results which is encountered. This is due in some part to the random nature of the molecular structure but may also be due to experimental variables which are difficult to control. Of these the more important are: non-homogeneity in the moulded sheet from which the specimens are cut, variations in the moulding procedure leading to differing amounts of strain from one sheet to another and variations in the sharpness of the cutting tool with which the specimens are cut. Homogeneity in the sheet may be ensured by moulding from a sample which has been compounded on hot mixing rolls, an antioxidant being added to protect the polythene. Freedom from moulding strains can be obtained by moulding the sheets at high temperatures and using no water cooling. The sheet if strain free will be dimensionally stable when heated to 130°C. For less critical purposes an annealing treatment, e.g. immersion in boiling water for one hour, will be of help. The last mentioned source of error, the cutting tool is the most troublesome. In the low temperature brittleness test big variations may be attributable to the bluntness of the cutting tool. No satisfactory solution has been found and constant attention must be paid to keeping the cutter sharp. An annealing treatment on the cut specimens will reduce the variability here also. The remarks on annealing, of course, are not applicable to extruded or moulded sections where one of the objects of testing is to reveal excessive processing strains.

Melt flow index (grade number or melt index)

A convenient property broadly indicative of the nature of a given polythene is one which can be generally related to the molecular weight. Such a property is the melt viscosity which has been used since the start of commercial production to classify a range of polythenes with reference to their molecular weights. It correlates roughly with a given level of physical properties and gives some indication of ease of processing. Since molten polythene exhibits non-Newtonian flow it is important to specify exact testing conditions and this has been done in two test apparatuses, the Williams plastometer¹ and the grader or melt indexer.^{2,3} The former is a parallel plate plastometer which was at one time widely used in classifying U.S. polythenes. It has now been generally replaced by the grader or melt indexer, which has always been used in Great Britain. This apparatus is in principle an extrusion plastometer, in which a piston under a load of 2,160 gm moves in a vertical metal cylinder containing molten polythene at 190°C and extrudes polythene through a tubular die. The basic features of the apparatus are shown in Fig. 11.1. The British and U.S. versions of the apparatus differ in some small details of dimensions but give substantially the same result. The possibility of producing a design of apparatus and a test procedure acceptable to both countries is being actively considered. The rate of extrusion from this apparatus in grammes per ten minutes is the figure

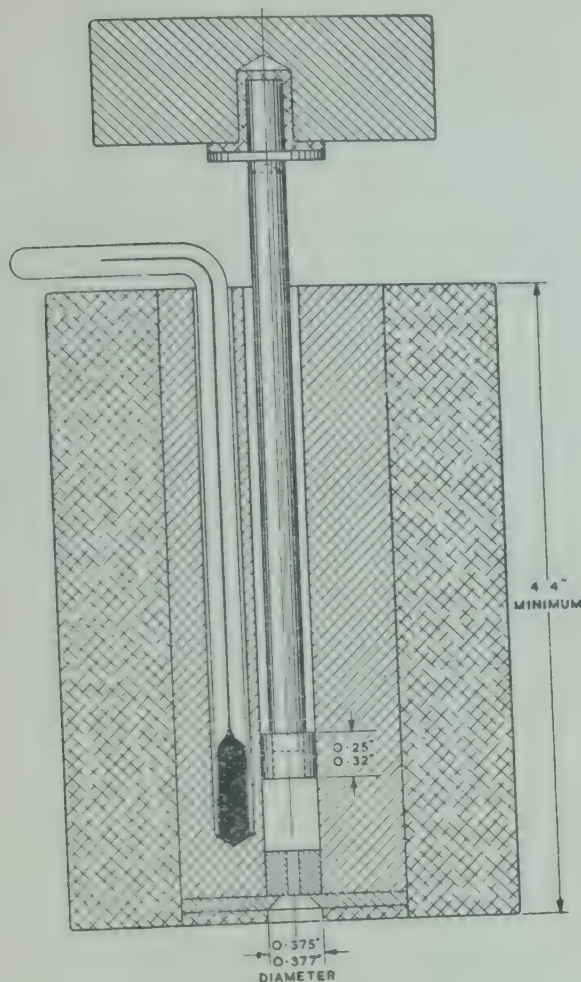


Fig. 11.1. Apparatus for determination of melt fluidity

used to characterize the polythene. This figure was known as the "grade number" in Great Britain and "melt index" in the U.S.A. A more descriptive term, "melt flow index", has now been introduced and will be the term adopted in this chapter. Measured on this test, the commercially available polythenes range from the high molecular weight material of melt flow index 0.2–0.3 (i.e., 0.2–0.3 gm extruded per ten minutes) used in submarine cable insulations through standard moulding, film and pipe materials in the 1.0 to 20 bracket to the soft materials used in wax blending and hot knife paper coating whose melt flow indices run into thousands.

Until recently melt flow index has been accepted as the unique characterizing test for polythene but the current trend is to attach less importance to it. This has followed from the realization that it does not completely fix the properties of a polythene and that it is perfectly feasible for two polythenes of identical melt flow index and density to have widely differing physical properties and flow properties, as, for example, the two polymers listed in Table 11.1.

The molecular weight distribution and the shape of the molecules,

Table 11.1 COMPARISON OF POLYTHENES HAVING SIMILAR MELT FLOW INDEX

Property	Polymer A	Polymer B
Melt flow index	2.0	2.1
Density	0.92 gm/cm ³	0.92 gm/cm ³
Intrinsic viscosity	0.85	0.84
Low temperature brittle point	< -70° C	-25° C
Solvent resistance (Bell test)	> 200 hr.	1 hr.
Vicat softening point	95° C	87° C
Relative rate of extrusion at high shear rates	0.36	0.78
Tensile strength	2,580 lb/sq. in.	1,900 lb/sq. in.
Elongation at break	630%	630%

no doubt, have a profound effect on the physical properties of the polymer. One may still observe a systematic variation of physical properties with melt flow index in a series of polymers all manufactured by the same process but in comparing two materials made by different manufacturers no such trends can be depended on.

For specification purposes, therefore, it may not be satisfactory merely to require a polythene within given limits of melt flow index but appropriate tests for the physical properties required in the particular application must also be included.

The melt flow index test was, of course, developed for use with polythenes of low density, i.e. 0.92 gm/cm³. In this material, experience has taught that, despite the differences between different polymers, certain melt flow index ranges are required for polythenes for certain applications, e.g. 2 to 7 for film and bottle manufacture, 10 to 20 for high speed injection moulding etc.

In the new polymers of densities up to 0.96 gm/cm³ there is no such background of experience, although melt flow index figures of less than 1 are being quoted for these materials. Needless to say, no similarities will be expected between two polymers of the same melt flow index but of differing density.

Tensile testing

Of the physical properties, some of the most commonly specified are the tensile properties and in particular the elongation at break and the ultimate tensile strength, i.e. the stress at break referred to the original cross sectional area of the specimen. In specifying the tensile properties of a plastics material it must be borne in mind that the appearance of the stress strain curve and the absolute values of the breaking stress are not simple properties of the material but can also depend on the previous thermal history of the specimen and on the rate of straining the specimens. The effect of the previous thermal history can be largely nullified by a conditioning treatment, for example, annealing the specimens for one hour in boiling water to remove moulding and extrusion strains. Because of the rate dependence of the tensile properties, it is necessary to specify the rate at which the test is to be carried out and also the exact dimensions

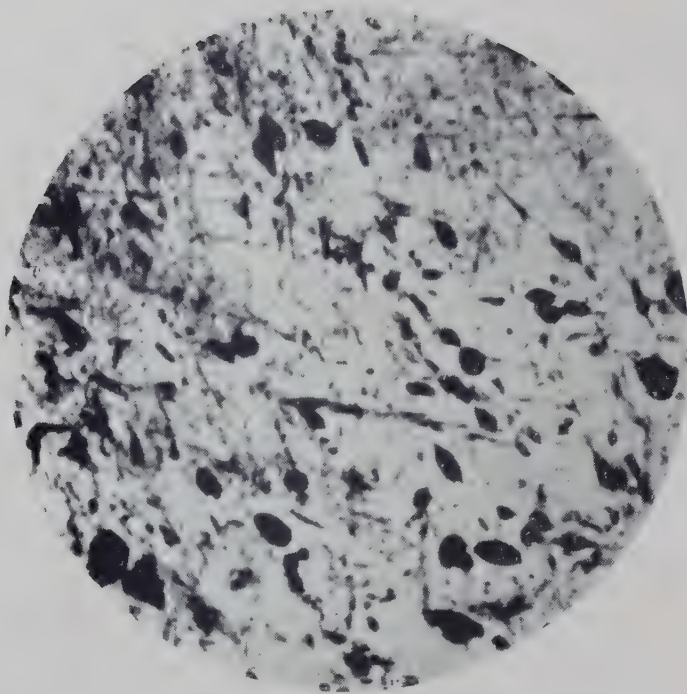


(a)

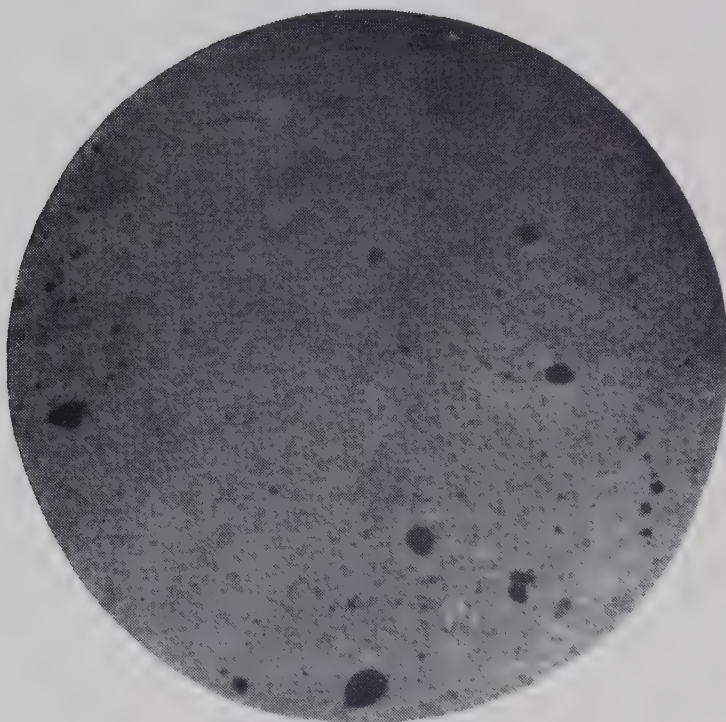


(b)

Plate 11.1. Dispersion of carbon black in polythene ($\times 200$)
(a) Dry tumbling in hopper; white areas are completely unprotected,
(b) Inadequate extruder homogenizing.



(c)



(d)

Plate 11.1

- (c) *Banbury homogenized compound with high carbon black agglomeration.*
(d) *Banbury homogenized compound of satisfactory quality.*

the specimen. The dependence of rate of testing on tensile properties assumes particular importance in the light of reports published of the tensile properties of some of the new high density polymers. One such material⁴ has an elongation at break of several hundred per cent if tested at 2 in./min. but a very low elongation, less than 100%, if tested at 20 in./min. The U.S. tensile test for plastics⁵ is quite impractical for polythene as each specimen would take many minutes to break at the specified speed of $\frac{1}{4}$ in. per minute. More suitable are the U.S. and British rubber tensile tests^{6, 7} which stipulate testing speeds of 20 in. and 18 in./min. respectively.

The choice of the ultimate tensile strength as an important property is at first sight obvious but a good case may be made for the use instead of stress at the yield point. Although for many polythenes these two stresses are essentially the same, for the higher molecular weight resins a further increase of stress occurs after a considerable amount of cold drawing. The effective upper limit to the stress that could be tolerated by an article is that beyond which permanent deformation occurs, i.e. the yield point. Therefore for many applications it is preferable to specify the yield point. In highly oriented specimens such as those cut from extruded film, however, the yield point is ill defined in the stress strain curve and the nearest approach is to record the cold drawing stress.

The importance of elongation at break is greater than is generally realised. The performance of a specimen under conditions of uniaxial strain is reflected in its performance under polyaxial strains. The bursting strength of a pipe, and the tear resistance of a film are properties which can be correlated with elongation at break. It is essential that tensile testing be carried out on the specimens cut from the completed article as well as on the specimens moulded from the original granules since poor extrusion can lead to severe local strains resulting in low elongation at break figures despite the use of good material. These local strains lead to brittleness in the extruded section and in a pipe, for example, would give a poor bursting strength.

Measurements of Young's modulus for polythene are complicated since this property is not a constant for the material. It depends not only upon the specimen shape and rates of strain as do the other tensile properties, but also, since the stress-strain curve for polythene appears to have no linear portion near the origin, it depends on the exact moment chosen for measurement. Nevertheless, the desire to exploit the improved stiffness of high density polythenes will arouse much interest in methods of measuring modulus. It is desirable to measure modulus in tension thus avoiding the necessity for a new test. A measure of a modulus nearly related to a true Young's modulus can be obtained by drawing the tangent to the stress-strain curve at the origin, or more precisely by drawing tangents at a number of points of low elongation and from the relation between modulus and strain extrapolating to a modulus at zero strain. A more practical test, however, is to define the modulus relative to a given percentage elongation as is the practice in rubber technology.

A 5 or 10% modulus is probably suitable for polythene. (See Chapter 9)

Modulus may also be measured in bend on a cantilever. In this type of test, again, the testing conditions must be specified in detail since they will have considerable influence on the result. The time to elapse before measurement must always be quoted in association with such a modulus since the creep of the polythene will give a constantly increasing amount of bend.

The tensile properties of a given manufacturer's polythene usually improve with decreasing melt flow index, e.g., the tensile strength and elongation at break of material of melt flow index 2 will be higher than that of melt flow index 20 from the same manufacturer, but this correlation cannot be made in a comparison of two manufacturers' materials.

*Environmental cracking**

A common reason for specifying a material of low melt flow index is to ensure the maximum protection against environmental cracking, the physical failure to which polythene is susceptible when stressed poly-axially in contact with certain organic solvents, liquid detergents, etc.⁸ In assessing the likelihood of this form of failure occurring three factors must be considered; the activity of the cracking medium, the resistance of the polythene and the applied stress, whether applied externally as in squeeze bottles, or as processing stresses, as in injection moulded articles. Unfortunately, in the present state of knowledge, there is no quantitative means of assessing the last mentioned factor but there is a test for comparing the resistance of different samples of polythene in a standard cracking agent and for comparing the activity of different cracking agents on a standard polythene sample.

This test is that developed in the Bell Telephone Laboratories⁸ in which a specimen 1.5 in. \times 0.50 in. \times 0.125 in. with a razor cut 0.75 in. long and 0.020 in. deep running centrally, parallel to the longer side, is bent into a U shape and constrained in a Pyrex tube 16 mm. internal diameter. The specimen is bent with the razor cut on the outside and exposed to the cracking agent at a temperature of 50°C. It is usual to test about ten specimens and having examined them at frequent intervals to report the time at which 50% of the specimens have failed. If it is the polythene which is being tested, an active cracking agent should be used in order to reduce the time of testing as much as possible. The cracking agent specified by the Bell Telephone Laboratories is a synthetic detergent, Igepal CA or Antarox A 200 which is an alkyl aryl polyethylene glycol ether. In this country there has been wide experience with Lissapol N a non-ionic detergent. With Lissapol N, figures of from one to four hours are obtained with the most widely used polymers in the melt flow index range 1-8 whilst cracking is unknown in some of the hardest materials, e.g. 0.2. The normal period of duration of the tests is 300 hours and if more than 50% of the specimens survive for this period it is usual to quote the percentage failure in 300 hours.

* See also Chapters 9 and 10

This test of course, imposes a more severe strain than is encountered in service. The applied strain at the base of the cut is very large and the temperature of test is higher than that normally encountered in polythene applications. The test therefore has no quantitative correlation with service conditions but can be of value as a relative measure. One can say with some confidence that a material which shows no failure in this test after 300 hours would be completely trouble-free in contact with the test liquid. The importance of sample preparation in this test cannot be overstressed. The sample should be cut from a strain free moulding with a sharp cutter (cf. Chapter 28).

Because of some unaccountable fractures during ageing and creep tests, the stress cracking of high density polythenes has also been investigated¹⁹ at elevated temperatures. These tests have been carried out using a miniature Bell Telephone Laboratories' environmental stress cracking test in which the dimensions of the apparatus and specimens were exactly half scale. Instead of a surface active agent environments such as air and distilled water have been used, and some very startling results obtained.

When high density polythenes are maintained under stress at a temperature of 80°C they develop cracks more quickly than low density polythenes and the higher the density the more rapid are these failures. Carrying out these tests *in vacuo* or with an anti-oxidant incorporated into the polymer does not make any significant difference, and it would thus appear that these failures are due to a so far undetected physical change which occurs at these elevated temperatures rather than to an oxidation effect. No change in crystalline structure has been detected but further investigation is in progress to determine the cause of these failures.

Low temperature brittleness

Brittleness of polythene at low temperatures is a property often included in specifications for polythene (See Chapter 9). The generally accepted method is the A.S.T.M. low temperature brittleness test⁹. In this test, rectangular specimens 1 in. × 0.25 in. × 0.075 in. are clamped at one end and the free end struck by a moving member travelling at a linear speed of 6–7 ft. per second. This blow is usually delivered by a motor driven rotating arm which is operated through a clutch. The specimen holder and specimens are immersed in a heat transfer medium, usually methanol cooled with solid CO₂. Ten specimens are tested at each temperature. Tests are carried out at 2°C or 5°C temperature increments over the range between the temperature of 100% failure and the temperature of no failure. The brittleness temperature, i.e. the temperature of 50% failure, is determined statistically by the formula.

$$T_b = T_h + \Delta T \left(\frac{S}{100} - \frac{1}{2} \right)$$

where: T_b = Brittleness temperature in degrees Centigrade.
 T_h = Highest temperature at which 100 % failure occurs.
 ΔT = Temperature increment.
 S = Sum of the percentage of breaks at each temperature.

In polythene there is a wide difference between the temperature which no failures occur and those at which failure is certain. This makes the determination of the low temperature brittle point a lengthy procedure since the material must be tested at frequent intermediate temperatures. However the complete test is not necessary for specifications and a pass or fail test based on this apparatus may be quite sufficient as a method of ensuring that the quality of a product is being maintained at an acceptable level. For example, a submarine cable specification requires that in 70 % of the batches there shall not be more than two failures out of ten tested at -76°C and that in 30 % not more than three. The unwieldiness of this clause is occasioned by the considerable statistical fluctuations of the test and allowance must always be made for this.

An alternative means of low temperature testing is used quite extensively for examining small diameter cable cores. In this a short length of the cable is wound round a mandrel of a specified size, e.g. ten times the cable diameter, both sample and mandrel having been conditioned for several hours at the test temperature. This test is usually specified requiring no failures at the temperature of test. It is a test extensively used in p.v.c. specifications but its validity for polythene has not been widely investigated. Along with all low temperature brittle tests, it is no doubt subject to considerable variability but it has the merit that, being on the fabricated sheath, it tests the quality of the extrusion as well as the raw material.

The application of a low temperature brittle test to the high density polythenes has not been closely investigated yet. The first results show figures on the A.S.T.M. test of the same order as have been obtained with conventional polymers yet it can be demonstrated that under a large impact some of the polymers being produced are brittle at room temperature. It has long been known that the low temperature brittle point was dependent on the conditions of test. It now seems likely that these differences will be of practical importance and that the existing test will not discriminate sufficiently amongst the wider range of polythenes now available.

Other physical tests

The above are the physical tests which can be generally used to characterize polythene. To these must be added density which has now become of increasing importance. The conventional methods of measuring density are suitable for polythene and have been closely specified by A.S.T.M.¹⁵ There are other tests which have special applications, such as tear strength of film, which are discussed below. In addition there are some gaps in the range of tests available in the present stage of

TESTING AND SPECIFICATIONS

development. The most serious omission is a test for examining the flow properties of polythene under high rates of shear. The extrusion conditions prevailing in the die of a polythene melt flow indexer are vastly different from those which exist, for example, in the die of a wire covering extruder operating at 20,000 yd./hr., so melt flow index is of limited value in assessing the processing properties of a polymer. There is no guarantee, polythene being a non-Newtonian fluid, that two materials which behave identically in the melt flow indexer will behave identically at high extrusion rates. Indeed there is no doubt that this is not true. The need therefore is for an apparatus, probably based on a similar principle to the melt flow indexer, i.e. ram extrusion, but which operates at very much higher shear rates by using higher pressures and a smaller die. Such apparatuses have been developed but there is as yet no generally accepted method of test which might be included in specifications.

The high density polythenes will introduce a need for a wider range of physical testing. In addition to density and stiffness, mentioned above, another improvement in these polymers which will be widely exploited will be a higher softening point. A useful test for the latter property is the Vicat softening point test in which a flat ended needle of 1 sq. mm. cross section under a load of 1 kg. penetrates into a polythene specimen under conditions of steadily increasing temperature (50°C/hr. in a glycerine bath). The Vicat softening point is the temperature at which the needle has penetrated one millimetre. The temperature recorded in this test is neither the true crystalline melting point of the polymer nor the practical upper temperature limit of utility of the material but is at least a relative indication of the latter. A speedy test for measuring crystalline melting point is not available, but would be a useful research tool in the future. An alternative softening point test, the A.S.T.M. Heat Distortion Test,¹⁰ may be of use in examining high density polythenes. It has been little used in the past since the flexibility of low density polythene even at room temperatures is so great as to influence the result considerably.

ELECTRICAL PROPERTIES

Power factor

The measurement of the power factor of polythene is one of the most useful tests available. It has a two-fold application in polythene specifications. Firstly, that polythene for use in a cable for high frequency radar and television applications must have a low power factor in order to have satisfactory electrical properties and secondly that power factor is a sensitive measure of the purity of the raw material. A high power factor in polythene is usually an indication of oxidation in the polymer either through maltreatment of the material during processing or through the use of poor quality scrap and rework material. Alternatively, it is an indication of the presence of excessive amounts of ionic impurities such as catalyst residues or pigments that are unsuitable for electrical

applications. In a cable sheathed with p.v.c., plasticizer migration in the polythene may also lead to a serious increase in power factor.

The tangent of the loss angle of a specimen of pure polythene will not exceed 0.0004 over the whole range from audio to microwave frequencies and even in a coloured material a specified figure of 0.0005 should be easily met if suitable pigments are used. Weathering grades incorporating carbon black, of course, have much higher power factors.*

The method of measuring power factor and permittivity of polythene is usually that developed by Hartshorn & Ward.¹¹ In this method the specimen is the dielectric in the capacitance element in a parallel resonance circuit. The polythene sample, which may be in the form of a tube or more usually a flat disc, is placed in the capacitance element of the circuit. The oscillator is tuned to resonance and the width of the resonance curve is measured as twice the capacitance change needed to detune the circuit to one half the maximum resonance value on the galvanometer. The width of the resonance curve is next measured with the specimen withdrawn from the apparatus and from these widths the dissipation factor, which is not significantly different from the power factor, and dielectric constant are calculated as follows:**

$$\tan \delta = K \frac{(W_p - W_a)}{2C}$$

$$\epsilon = \frac{144 d C}{D^2}$$

where: K = A constant for the instrument.

W_p = Resonance width with the polythene specimen present.

W_a = Resonance width with the polythene specimen absent.

C = Capacitance of condenser, determined from a calibration curve.

d = Thickness of test piece in millimetres.

D = Diameter of test piece in millimetres.

There is a formula to allow for edge corrections to the capacitor but this is not necessary except for the most precise measurements.

This apparatus can be used over the frequency range 10^4 – 10^8 c/s and a frequency in the region 10^6 – 10^7 c/s is best suited for routine testing. On pure unoxidized polythene figures of 0.0001–0.0002 will normally be obtained. The experimental error with such a low figure is considerable and may be as large as 0.00005.

For special applications, a specification sometimes calls for power factor measurements in the audio-frequency range. At these frequencies, with power factors of below 0.0001 occurring often, measurements are

* See Chapter 6.

** These formulae refer to disc specimens.

ery difficult. The sensitive Schering Bridge described below is a suitable instrument.

Dielectric constant

With the exception of specialized cable specifications where it is used as a definitive test of the material to be used, the dielectric constant of polythene is not a suitable property for inclusion in specifications. Its value is substantially the same for all grades and brands of polythene of low density and it is a property which is difficult to measure accurately. The Hartshorn and Ward set described above will give an accuracy no better than $\pm 2\%$ and only a gross amount of contamination would give even a 2% difference from the accepted value of 2.28. Contamination of this sort is anyway far more easily detected by power factor measurement. Although theoretically both power factor and dielectric constant can be measured on the Hartshorn and Ward set, in practice the use of tin foil electrodes which is essential for dielectric constant determinations is undesirable in power factor measurements. Two tests are therefore necessary.

The measurement of dielectric constant to a much closer precision is of importance in projects such as submarine telephone cables. These measurements are made in the audio-frequency range and dielectric constant measurements to an accuracy of ± 0.01 are now quite practical. Still more accurate methods are being developed.

The most popular instrument for audio-frequency measurement is the conjugate Schering Bridge, a three terminal bridge which is balanced first with the capacitor carrying the specimen in the circuit in parallel with one arm of the bridge and then without. Power factor and dielectric constant can be calculated from the balance conditions for the bridge. With this instrument capacitance can be measured to a high degree of accuracy and the limitation in determinations of dielectric constant is the difficulty of producing a sheet of polythene of sufficiently uniform thickness. It is usually necessary to use a statistical weighting technique to average the thickness measurements if high precision is required. The instrument is suitable for use in the frequency range 25 c/s to 5 Mc/s.

As well as the two discussed above, a number of other circuits suitable for studying the dielectric properties of polythene are described by the A.S.T.M.¹⁸

Looking to the future, polythenes of higher density will have an associated small increase of dielectric constant. However this will be fixed by the density according to the Clausius-Mossotti relation

$$\frac{\epsilon - 1}{\epsilon + 2} = K\rho$$

ϵ = Dielectric constant
 ρ = Density.

It does not seem likely therefore, that there will be a case for specifying

dielectric constant in general specifications provided that the much simpler density determination is included.

Resistivity

The volume resistivity of unpigmented polythene is so high, about 10^{19} ohm cms, as to be unmeasurable on standard equipment. Therefore volume resistivity itself is not usually a specified property. More usual is a requirement for insulation resistance on a completed length of cable. The resistance of the length of cable is normally measured from each strand to all of the others and from all the strands to earth. The figure to be specified will of course depend on the geometry of the cable and the resistivity of the coloured compound used in the cores, and will probably be fixed in the light of past experience on similar cables. An insulation resistance test will, of course, detect poor extrusions as well as faulty material.

In testing the resistance of polythene insulated cable it must be borne in mind that on the application of the testing voltage a polarizing current will flow in the circuit and that a relatively high current will be recorded initially falling off with time. Care must be taken not to flex the cable during testing, since current will flow whilst the capacity is changing. The attaining of a steady current may take several minutes and this should be allowed for in the specification.

THE EXAMINATION OF POLYTHENE COMPOUNDS

It is necessary for certain critical applications to examine the additives contained in polythene compounds. These compounds comprise weathering compounds whose efficiency depends on the quantity of carbon black included and the quality of its dispersion, compounds containing polyisobutylene or butyl rubber where dispersion and quantity are important, and compounds containing thermal antioxidants.

*Carbon black in polythene compounds**

Carbon black up to a concentration of 2–3% is incorporated in polythene in order to give protection against photo-oxidation by ultra-violet light.¹² A compound containing at least 2% carbon black is therefore widely used in outdoor applications such as pipe and cable sheathing where continuous exposure to sunlight is probable. It is, however, vital to the efficiency of such a compound that the carbon black should be uniformly dispersed. It is not an exaggeration to suggest that a poorly dispersed carbon black compound is little better as a weathering material than is natural polythene itself. Therefore it is essential that any specification for a weathering grade of polythene should include, in addition to a quantitative analysis for carbon black, an examination of the dispersion quality. This test can be carried out using microscope slides which are prepared either by pressing a small piece of the compound

* See also Chapter 6

between two glass slides on a hot plate or from a fabricated article by cutting a thin section with a microtome. The slide should be examined at least $100\times$ magnification. This slide must then be compared with a slide or microphotograph which is used as a standard. Some samples of carbon black dispersion are shown in Plate 11.1. Plate 11.1a is a dispersion of the type encountered when carbon black and polythene are dry tumbled in the extruder hopper; the white areas are completely unprotected. Plate 11.1b is typical of a compound prepared by inadequate extruder homogenizing of a blend of polythene and a carbon black master-batch. Plate 11.2c is of a Banbury homogenized compound with an undesirably high number of carbon black agglomerates. Finally Plate 11.2d, represents a commercial Banbury homogenized compound of satisfactory quality. It is to be regretted that this type of test is a highly subjective one but such a test has been operated successfully for several years and agreement between different examiners is remarkably good. Alternative tests based on photometric measurements have not been adopted in this country although they are now being quoted in America. The apparatus used is the integrating sphere photometer.¹³

The best method for the quantitative determination of carbon black in polythene is a gravimetric one. The sample is heated in a porcelain boat up to a temperature of 500°C in a continuous nitrogen stream. At this temperature the polythene pyrolyzes, the pyrolysis products are removed by the nitrogen stream and the residual carbon black is weighed. A sample of 1 gm of compound is sufficient for an accurate determination.

*Butyl rubber in polythene compounds**

Butyl rubber or alternatively polyisobutylene is added to some polythenes in order to improve resistance to environmental stress cracking. The compounds are used in particular for cable sheaths and for pipe where an environmental cracking hazard exists. A good dispersion of the rubber is necessary since undispersed rubber, as well as introducing inhomogeneity, means less rubber than has been specified in the remainder of the compound. The dispersion of a compound can be simply examined in a moulded sheet about 0.050-in. thick. When this sheet is held to a light, undispersed rubber particles stand out as discrete transparent areas, known as "windows". There should be no "windows" in a good quality compound.

For the quantitative analysis of butyl rubber in polythene, a 1 gm sample of the compound is dissolved in hot toluene. The polythene is precipitated from the hot solution by the addition of petroleum ether, the rubber remaining in solution. The precipitate is filtered off, the filtrate evaporated to dryness and the butyl rubber residue weighed. The filtrate contains also a small amount of the low molecular weight fraction of the polythene so it is necessary to do a control experiment, ideally on a sample of the actual polythene from which the compound has been made, or

* See Chapter 25 and Chapter 28.

more practically on a sample of polythene of the same melt flow index from the same manufacturer.

The remarks in the section apply equally well to butyl rubber or to polyisobutylene.

*Antioxidants in polythene**

Antioxidants are included in polythene to give protection to the material against thermal oxidation which occurs at a measurable rate at elevated temperatures. There are three stages at which the polythene may be exposed to these elevated temperatures; during the manufacture of the compound, during the extrusion or moulding of the fabricated article and during the life of the fabricated article. The last of these occurs only in a few special applications since the oxidation process at room temperatures is negligible. There are, however, certain polythene articles which will encounter temperatures of 60°C and above, e.g. polythene pipe or cables exposed to tropical sunshine or cables subjected to heavy surge currents. In specifications for such applications it is necessary to require the finished cable, pipe, etc., to retain the optimum quantity of antioxidant. This will mean that the manufacturer of the compound must add excess antioxidant to his mix since some will be consumed during compounding and extrusion.

For applications where no high temperatures are to be encountered in service, it is only necessary to ensure that the polythene has not suffered from oxidation during fabrication. This may be done by specifying an analytical test to detect a nominal residue, say 0.02% minimum, of antioxidant in the finished article or by requiring certain physical and electrical properties to be unaltered at the end of the manufacturing process. If the latter course is to be adopted, by far the most useful property to examine is the power factor which is the most sensitive test of the oxidation of polythene. Power factor examination however, cannot be used in carbon black compounds where the power factor is high initially.

Similarly in specifying tests on the compound as supplied there are two possibilities, an analytical test to detect the required amount of antioxidant or tests to show that the properties of the compound remain unaltered by a severe heat treatment. An example of the latter occurred in an important cable specification where the compound was required to pass the same tests after three hours on mixing rolls at 150°C, as it had to pass before this heat treatment.

There are three antioxidants currently used with polythene in this country although others are used abroad and the manufacturers are constantly examining new possibilities.

The three antioxidants at present widely used are di-*o*-cresylol propane, NN'-di- β -naphthyl-*p*-phenylene diamine and NN'-di-phenyl-*p*-phenylene diamine. Of these the first named is used because of its non-staining properties but the latter two which stain violet and brown respectively

* See also Chapter 6.

the superior antioxidants and should always be specified where protection during service is required. The naphthyl derivative is specified in the British Standard for polythene cold water pipes.² The di-phenyl derivative has been called for in several U.S. cable specifications. The quantities usually recommended are 0.07% for di-phenyl-*p*-phenylene diamine and 0.1% for the other two antioxidants. These figures are fixed by the tendency of the antioxidants, if in excess, to bloom out of the compound forming a fine powder on the surface of the extrudate or moulding. Apart from its unattractive appearance, this bloom can be troublesome, e.g. in a cable core which has to be subsequently sheathed with nylon.

Analytical methods have been developed for all three antioxidants. They are all colorimetric methods. The compound is dissolved in toluene, the antioxidant converted into a distinctively coloured derivative and the optical density of the colour in the solution measured with a Spekker absorptiometer. The measured optical density is compared with a calibration curve based on solutions of known concentration. As an alternative to this expensive apparatus, coloured comparator discs are available for di- β -naphthyl-*p*-phenylene diamine solutions and this technique could be extended to the other antioxidants if necessary.

THE TESTING OF FABRICATED POLYTHENE

Most of the tests described above were developed for the examination of polythene or polythene compounds as supplied but many of them are also used in the examination of polythene cable, film and pipe. Specifications for these articles may also include tests adopted from those used for other materials, e.g. the Elmendorf paper tear-testing machine which is widely used in the evaluation of polythene film.

The testing of cables

It is usual in cable specifications to require almost all the polythene tests to be carried out on the sheath itself rather than sheets moulded from it. This enables the examiner to check the quality of the extrusion as well as of the material. In particular the cable-maker should have avoided areas of local strain which will lead to a low elongation at break and a poor performance at low temperatures. This is distinct from the overall longitudinal strain which can be measured by heating a sample of the core, the conductor having been removed, at a temperature of 130°C for one hour. The sample should be laid on a bed of talc or be floating in oil. A maximum value for this property has on occasion been specified but there are little grounds for this. All experimental attempts to show a correlation between the physical or electrical properties of a sheath and the high temperature retraction have yielded no positive results. A polythene insulated cable will always pass a "hot-shock" test of the type sometimes specified for p.v.c. sheathings, and this type of test for polythene is therefore of little value.

The electrical tests are usually carried out on completed length of cable and the methods used are those standard in the cable industry. The effect of polarization currents in prolonging the time required for accurate resistance measurements has been mentioned above.

The testing of pipe

Probably the most important aspect of tube specifications is the examination of carbon black dispersion in black pipe. The difficulties involved in specifying this test have been discussed above. The use of a standard microscope slide or microphotograph is becoming generally accepted.

The remarks about local extrusion strains in the preceding paragraph apply equally well to polythene pipe testing and tensile tests on specimens cut from the wall of the tube are normally included in specifications. An elongation at break of not less than 350% should not be difficult to meet. A uniaxial tensile test of this type cannot, in the present state of knowledge, be correlated directly with the performance of the tube in service under hydraulic pressure. It is therefore necessary to test the tube under a given pressure usually about twice as high as the maximum working pressure. The bursting pressure of a polythene tube in a short term test will be very different from that under a constant pressure applied over a long period, the latter of course being the service conditions. The difference is due to creep in the polythene under load leading to thinning of the walls. From experimental measurements of creep, it is possible to deduce a short term testing pressure which will guarantee a long life to the tube at the working pressure, the creep being sufficiently small to be ignored.

The testing of film

Although there are no widely used specifications for polythene film, manufacturers doubtless have their own internal requirements which will be used, probably, as a basis for a generally accepted specification in due course. The testing of polythene film differs considerably from that of polythene in other forms. In film, visual appearance is of considerable importance and any specifications would require certain standards of light transmission and freedom from haze. Another property of considerable importance to the manufacturer is "blocking" i.e. the tendency of the two sides of lay-flat tubular film to adhere to each other. This causes considerable inconvenience to the fabricator of polythene bags who must be able to open the tube readily. Blocking is not an easy property to assess quantitatively but tests have been proposed based on the force necessary to open the tube.

The mechanical properties of polythene film must also be considered. Before discussing these, it should be pointed out that all extruded polythene film contains a considerable amount of molecular orientation. This is uniaxial in wide film and biaxial in tubular film and the actual

* cf. Chapter 27.

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amount of the anisotropy can be varied by altering the extrusion conditions. Much of the art of tubular film manufacture lies in obtaining an even balance in the properties of the film. It is necessary, therefore, to carry out all measurements of the physical properties in two directions, parallel to and perpendicular to the direction of extrusion. Substantial differences may be found between the two directions. In addition to tensile tests, there is a need for a test to measure the tendency of a film to tear when subjected to sudden localized load, such as occurs when a polythene bag is filled with, for example, vegetables. An attempt has been made to use the Elmendorf tear test for polythene film. This is a test used in the paper industry. A cut is made in a rectangular test specimen parallel to the long sides and along half the length of the specimen. One of the "trouser legs" so formed is fixed in a clamp attached to the back of the apparatus and the other in a clamp on the end of a loaded pendulum which is pivoted in the centre and held horizontally. The pendulum is released and the energy lost in tearing the specimen is measured from the size of the first swing of the pendulum. The disadvantage of this test has been shown to lie in the relatively slow rate of propagation of the tear. Polymers with high Elmendorf tear strengths have been found to be brittle in service when subjected to sudden loads. A more successful line of approach will probably be a test of the type of the falling weight impact test and some have been proposed. The load may be dropped on to a piece of film clamped taut like a drum; a test in which a polythene bag containing a known weight of sand is dropped from successively increasing heights has proved quite useful.¹⁴

SPECIFICATIONS FOR POLYTHENE

It has been mentioned in the early parts of this chapter, that in the past a great deal of emphasis has been laid upon melt flow index as the test to determine the polythene for a given application. This is illustrated in the existing specifications for polythene products where the usual practice has been to specify precise limits for melt flow index whereas for the remaining properties there are specified numerical limits which could be met by any polythene which has not been grossly maltreated. This state of affairs has developed largely because of the small number of polythene manufacturers during these years, one in Great Britain and two in the U.S.A. In the war period, when polythene was available only for defence purposes, the cable trade were quite satisfied in their specifications to call simply for a melt flow index test with a few quality control tests. As there were so few suppliers and only one type of material of a given melt flow index was made by each manufacturer, the melt flow index alone was sufficient to define the material. The actual melt flow index limits specified follow the commercial practices of the supplier. This can be illustrated by two well known specifications. The British Standard for polythene tube for general purposes¹⁵ quotes

three grades of polythene defined by the melt flow index limits 1.7-2.6, 6-8, and 17-23 and the U.S. polythene material specification¹⁶ define three general purpose grades based on limits 2.3-5.2, 1.3-2.7, 0.8-1. In both cases these limits conform to the existing commercial range in the country concerned.

Developments, both commercial and technical over the last two years will almost certainly lead to a radical change in the approach to specification.

Many new manufacturers all over the world have started or have announced their intention to start producing polythene, individual manufacturers are developing new polymers which although of the same melt flow index show different properties from their normal range, and polythenes of high density which have melt flow indices in the normal range yet have vastly different properties are making their appearance. Melt flow index, therefore, can no longer be regarded as a unique characterization test. What is to replace, or more probably to supplement it, is open to speculation. Certainly as polythenes of a wide density range e.g. 0.92-0.96 gm/cm³ become available, tight limits of density will need to be specified. What does seem probable is that the approach to the writing of specifications will have to be reversed. Instead of specifying a narrow range of melt flow index in the sure knowledge that this will mean certain physical properties, it will be necessary in future to specify the actual properties required of the material, still retaining melt flow index as a general guide to the properties but allowing a wide range since, for example, whereas one manufacturer will offer material of melt flow index 2 to meet a certain clause of the specification, another may need to offer material of melt flow index 1.

Specifications for polythenes are published by national bodies such as the British Standards Institution, the American Standards Association and the American Society for Testing Materials, by government departments including the armed forces, and by trade associations. These generally are specifications for the completed articles but often include tests on the raw material as supplied. A need for a comprehensive material specification defining polythenes suitable for the various applications is becoming increasingly apparent and is being given active consideration on both sides of the Atlantic. The American Society for Testing Materials have made the first attempt at such a specification although the requirements are not closely defined except for melt flow index.¹⁵ This specification describes two types of polythene, a general purpose material which is divided into three grades based on melt flow index determination i.e. 0.8-1.6, 1.3-2.7 and 2.3-5.2 and a dielectric material of melt flow index 0.8-2.1; the latter may be natural, coloured or general purpose black. The quantity of black included in the last mentioned is not specified but it is intended as an insulation grade and a minimum volume resistivity of 10¹³ ohm cms is required. For all grades density and tensile tests are also required and for the dielectric materials (not black) brittle temperature, power factor and dielectric constants are

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cluded. A.S.T.M. test methods are called for all testing but the limits imposed are not a severe requirement.^{3, 6, 9, 17, 18}

It is the common practice in both the U.S.A. and Canada to refer to this specification to define the polythene to be used in any other specialized specifications.

Existing specifications for polythene and polythene products

This list is by no means a complete one. It includes all the more important British and U.S. specifications and examples of the wide range of polythene products, particularly in the cable industry, for which specifications have been published.

Great Britain

- B.S. 559 (British Standards Institution): "Electric sign and high voltage luminous discharge tube installations."
- B.S. 1557 (British Standards Institution): "Polythene insulated cables sheathed with p.v.c. for electric power and lighting up to 250 volts."
- B.S. 1972 (British Standards Institution): "Polythene tube for cold water services."
- B.S. 1973 (British Standards Institution): "Polythene tube for general purposes including chemical and food industry uses."
- B.S. 2456 (British Standards Institution): "Floats for ball valves (plastics) for cold water."
- D.E.F. 10 (Ministry of Defence): "Miniature electric cables."
- D.E.F. 12 (Ministry of Defence): "Equipment wires."
- D.E.F. 14 (Ministry of Defence): "Radio frequency cables."
- G.D.E.S. 27 (Ministry of Supply): "Polythene insulation and sheathing from electric cables."

United States of America

- A.S.T.M. Specification D.1248-52 (American Society for Testing Materials): Polyethylene moulding and extrusion materials."
- American Standards Association: "Weather-resistant wire and cable, polyethylene type."
- Insulated Power Cable Engineers Association: "Specification for wire and cable with polyethylene insulation."
- Rural Electrification Administration PE14—"Plastic insulated, plastic sheathed telephone cable."
- MIL-D-3054A: "Dielectric material polyethylene."
- MIL-P-3803: "Plastic, polyethylene, moulded and extruded shapes, sheets and tubing."
- MIL-C-10581A: "Cable telephone; cable assemblies, telephone, coil assembly, telephone loading."
- MIL-C-15479B: "Cables, power, electrical, submarine, Navy standard harbor defense."

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- USA No. 71-3266 (U.S. Army): "Wire WD-1/TT, infantry field wire, twisted pair."
- JAN-C-17A: "Cables, coaxial and twin conductor for radio frequency."
- CS 197: "Dimensions and tolerances for flexible standard wall polyethylene pipe."

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16. "Polythene moulding and extrusion materials", A.S.T.M. Specification D1248-52T.
17. "Specific gravity of plastics: Method B", A.S.T.M. Method D792-50.
18. "Power factor and dielectric constant of electrical insulating materials", A.S.T.M. Method D150-47T.
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LOW MOLECULAR WEIGHT POLYTHENE

D. G. THORNLEY

THE bulk of the polythene made throughout the world is extruded or moulded. The polymers which have been described in the preceding chapters have molecular weights between 18,000 and 50,000 and melt flow indexes between 0.2 and 20. There are however, polythenes of low molecular weights with consistencies ranging from that of oil and grease to hard wax. Most of them are made by the high pressure technique but at least one product made by a low pressure technique has been announced.

The high pressure method can be used to produce a range of these lower molecular weight types which appear at one end of the scale as oils and greases and at the other end with increasing molecular weight, as waxes. The products have a structure consisting of straight hydrocarbon links with a few branches. A hard waxlike low molecular weight polythene (3,000) of low density can have a melting point of about 110°C almost as high as the high molecular weight types (ca 20,000), but a melt viscosity of 1–10 poises compared with 10,000–100,000 poises for the high molecular weight polymer.

The relationship between chain length and crystallinity and the nature of the resulting polymer is shown graphically in Chapter 9 (Fig. 9.1, p. 141). Most commercial polythenes used in the plastics industry lie within the small shaded band in the centre of the diagram. The polythenes which are the subject of this chapter lie in the area to the left of a line drawn vertically from the point 10,000 marked on the molecular weight axis. Polymers in this area are liquids, greases and waxes. The properties of the two types of low molecular weight polythenes manufactured by the high pressure systems vary in degree rather than in character. These two classes will be referred to as low density polymers and high density polymers respectively.

Low density low molecular weight polymers have molecular weights lying in the range from 1,000 to 13,000 and a crystallinity of about 60%. In certain respects they behave similarly to the low density polythenes of higher molecular weight, and their melting points are of the same order, 110°C . Their densities do not exceed 0.92 gms/c.c. On the other hand, because they have lower molecular weights, there is a marked falling off in mechanical properties. Typical values of some of the chief properties of these types of polythenes are given in Table 12.1 overleaf.

As seen, the electrical properties of these polymers, except at the lowest end of the range, are as good as polymers of high molecular weights.

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Table 12.1. AVERAGE PROPERTIES OF LOW DENSITY LOW MOLECULAR WEIGHT POLYTHENES

Melt flow index	700	2,000	7,000	20,000	70,000	200,000
Molecular weight ^a	9,000-13,000	7,000-11,000	5,500-9,000	3,500-7,500	2,000-5,000	1,000-4,000
Brittle point ^b (°C)	-20 to -30	-20 to -30	-20 to -30	—break	at room temp.	—
Vicat softening point ^c (°C)	50-70	35-58	28-46	20-34	soft at room temp.	—
Freezing point (°C)	100-106	96-102	92-98	86-94	78-88	below 8
Tensile strength ^d (lb/sq.in.)	750-925	650-750	425-650	275-500	150-300	<150
Extension at break %	45	40	30	20	<20	<20
Density (gm/c.c.)	0.905-0.915	0.900-0.910	0.895-0.905	0.885-0.900	0.875-0.895	0.865-0.885
Power factor ^e (tan δ at 16 Mc/s)	<.001	<.0015	<.002	<.004	<.01	<.01
Permittivity ^e (ε)	2.25 - 2.30					

^a From intrinsic viscosity measurements in tetralin solution.

^b Temperature at which annealed half-dumb-bell specimens 2.5 mm × 12.5 mm × 1.6 mm thick have an even chance of breaking when bent round a mandrel 8.0 mm diameter.

^c Temperatures at which a needle 1 sq.mm square section under a load of 1 kg penetrates specimen to a depth of 1 mm. Rate of heating 50°C/hour starting below 30°C.

^d Specimens 1 in. gauge length annealed for 10 min. at 100°C; tested at 20°C rate of extension 4 in. per minute.

^e Determined on N.P.L. Type Dielectric Test Set.

The molecular weight of high density low molecular weight polythenes generally lies between 3,000 and 7,000. Being more crystalline they have a higher density of about 0.93 gm/c.c., and their melting points are sharper and higher at 112°C-115°C; in addition the melt is more mobile as they have lower melt viscosities. They are harder, brittle and are easier to blend with other types of waxes.

Not much is known about linear polymers of low molecular weight manufactured at low pressure but they will probably resemble the high density low molecular weight polymers mentioned above.

Finally there are the emulsifiable low molecular weight polythenes which have been modified during manufacture so that stable emulsions can be produced using methods similar to those used for natural waxes, but at slightly higher temperatures. One such modification is to introduce free acid groups into the polymer molecule.

All low molecular weight polythenes; have exceptional resistance to the action of acids, alkalies and aqueous salt solutions and are insoluble in water, very sparingly soluble in cold organic solvents, but soluble at about 70°C in hydrocarbons and chlorinated hydrocarbons (see chapter 10).

Like other members of the polythene family, these polymers are also subject to oxidation at elevated temperatures. This degradation of the polymer is accompanied by a change in physical and electrical properties.

LOW MOLECULAR WEIGHT POLYTHENE

The thermal oxidation of these polythenes may be reduced or arrested for a time by the addition of a suitable antioxidant, generally a member of the phenol or amine group (see chapter 6).

APPLICATIONS

These polythenes are used when materials of low softening points and low melt viscosities are required and when their weak mechanical properties can be tolerated. They can be used either by themselves or blended with paraffin waxes or as emulsions in water or solvents.

Low molecular weight polythenes are used in blends with paraffin or micro-crystalline waxes for coating paper for wrapping bread, sweets, etc. They are compatible with most of the vegetable and mineral waxes so that, by using hot mixing equipment of the Baker-Perkins type, blends of varying ratios of polythene to natural wax can be successfully made. This has proved to be a relatively large outlet due to the spectacular rise in prices of imported vegetable waxes. Polythene/wax blends may be used in applications which are normally barred to paraffin waxes alone because of improved appearance, increased toughness, reduction in brittleness and less tackiness.

A range of these polythene/wax blends with various properties may be produced by adjusting the ratio of polythene to wax. Increasing the polythene content will produce a harder wax finish with better gloss and more abrasion resistance, but will raise the melting point and melt viscosity of the blend.

Emulsifiable polythenes are of interest for emulsion polishes. These polishes previously contained hard wax or waxes in addition to the cheap paraffin wax. When the emulsifiable polythenes were developed it was found that if they were introduced as a substitute for the hard waxes in these polishes, the properties of the resulting paste were not impaired. A typical formulation for such a polish is:

	%
Emulsifiable polythene	8
Oleic acid	1.4
Triethanolamine	0.8
Potassium hydroxide	0.2
12% shellac solution	17
Water	72.6

In emulsifying the polythene, either the wax may be added to the water or the water may be added to the wax. There is a slight difference in technique depending on the method used. In the case of the wax to water method, the wax and oleic acid are first heated to 115–120°C with stirring, the potassium hydroxide dissolved in a minimum of water then being added and the mixture stirred until foaming ceases. The amine is then added and the mixture heated at 110–115°C for 15 minutes. Finally, the molten wax is rapidly poured into hot water (95°C) with vigorous agitation and, when the emulsion has formed, the shellac solution is

added and the emulsion rapidly cooled to room temperature. After the emulsion has been allowed to stand for 24 hours it is filtered.

These polythenes may also be produced in the form of an aqueous dispersion and in this form they can be applied by means of the conventional spray gun. They can also be applied by roller and even by hand brushing. After application, the polythene coating has to be fused generally by passing the coated material under heating elements. Heating by infra-red rays is a conventional method. The recommended temperature of fusion is 150°C (see chapter 23).

Other uses which have been suggested for low molecular weight polythenes are glass coating, fruit coating, leather finishes and dressing wire and cable insulation, gelling agents, ingredients for printing inks, carbon paper backing, candles, lubricants for plastics, carriers for pigments, mould release agents, oil additions, water-proofing and, in the cable trade, the bonding of oils as a filling for terminal junction boxes.

COATING TECHNIQUES

The usual techniques used in the wax paper coating industry may also be employed for coating paper with polythene/wax blends. These hot melt coating machines are based on the conventional coating equipment used for aqueous or organic solvents coatings. Because the melt viscosity of polythene/wax blends is sensitive to small changes in temperature, an important part of the design of any hot melt coating machine must be the inclusion of an accurate method for the careful control and maintenance of the temperature of the coating. Again, it is generally necessary to cool hot melt coatings before the paper can be rewound on to rolls and so most paper coating layouts will include a zone where the coated paper will pass over water-cooled rolls. In some cases where a tacky blend is being used, an additional cooling system is introduced in which cold air is blown upon the coated paper at high velocity before passing over water-cooled rolls. The common types of hot melt coating machines can be classified under three headings according to the basic principle on which they work, namely: knife coaters; roller coaters; reverse roll coaters.

Knife coaters. This type of coating machine is probably the oldest in design. Its main advantages are simplicity and low cost. There are



Fig. 12.1. Chief types of knife coaters: left, the knife-roll and, right, inverted knife with transfer roll

several variations of basic arrangement, but the two which are most commonly used for hot melt coating are the knife-roll and the inverted knife with transfer roll. These are illustrated in Fig. 12.1.

The knife roll coater can be used with coatings of high viscosities which the inverted knife and transfer roll type cannot handle. On the other hand the inverted knife and transfer roll machine can be equipped with a heated pan to maintain close control over the temperature of the coating blend.

Knife coaters suffer from the serious disadvantage of being inaccurate in control of coating thickness due to the thickness being affected not only by the clearance of the knife above the paper and the pressure upon it, but also by the thickness of the paper and the viscosity of the melt. Streaks may also occur in the finished coating caused by any variation in consistency or the presence of foreign particles in the coating blend.

Roll coaters. These machines are generally used with coating blends of relatively low viscosities. There are several basic types, two of the commonest being shown in Fig. 12.2.

In these machines the coating and transfer roll are heated. The two roll vertical type coater can be used for applying coatings to both sides of a web simultaneously by pumping part of the coating blend to the top side of the web as it enters the roll. By the use of precisely ground chilled

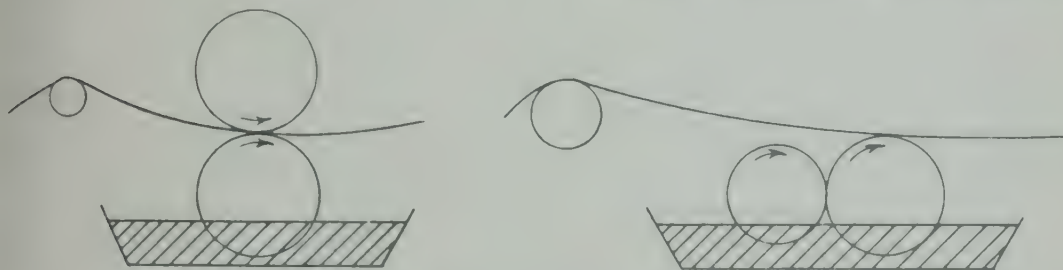


Fig. 12.2. Two of the most common arrangements for roll coaters

iron coating rolls very accurate coating weights can be applied subject to variations in the thickness of paper. On the other hand roll coaters are apt to produce a ribbed finish unless stationary smoothing bars or smoothing rolls, which are driven slowly against the travel of the web, are introduced into the process. When the viscosity of the blend and the speed are increased, there is a tendency for a build up in fluid pressure between the rolls, giving a coating of varying thickness. This may be overcome by using crown rolls; but this reduces the flexibility of the machine, as the rolls can be ground only to suit one set of conditions.

Reverse roll coaters. The reverse roll coater was designed to overcome the several disadvantages of the knife and roll coater. The coating is applied to the paper by means of a casting roll travelling in the opposite direction to the paper. The thickness of the coating on the casting roll is controlled by a metering roll travelling in the opposite direction to the casting roll and the final thickness of the coating on the paper is increased

in relation to the speed ratio of the casting roll to the paper. Two arrangements of this type of coater is shown in Fig. 12.3.

If the backing roll of these machines is covered with a synthetic rubber the roll should be internally cooled with water. A metal backing roll may be used when a very uniform or thick web is being coated.

Reverse roll coaters give a precise coating and because the roll surfaces travel in the reverse direction to each other, there is no fluid pressure between them and therefore the rolls may be ground with a straight face without crown. Their main disadvantage is a limitation on top speed.

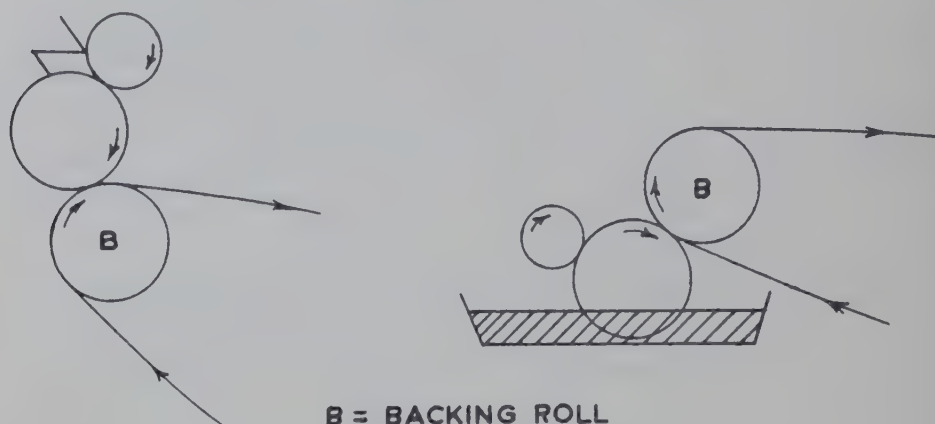


Fig. 12.3. Two arrangements for reverse roll coaters

due to the shearing of the coating and a minimum practical wet thickness of coating of about one mil.

There is no doubt that these polythenes are now established in the wax industry, especially in the United States where much more development work has been carried out than in Europe. They are now recognized as cheaper substitutes for the expensive hard waxes which before the war had a world production figure of between 30,000 and 40,000 tons per year. This perhaps is their biggest outlet; but the market for such polythenes compared with the other polythenes or other plastics is small and they probably will always represent a minor proportion of polythene consumption.

CHAPTER 13

IRRADIATED POLYTHENE

A. CHARLESBY

OF the many long-chain polymers which crosslink when subjected to high energy radiation, polythene has received by far the greatest amount of attention. Polythene appears to be one of the simplest of readily available polymers which crosslink and a great deal of scientific data has already been accumulated as to its physical properties in the absence of radiation. The improvement in these properties, particularly its thermal stability, which result from radiation promises to extend its range of application into new fields.

The apparent simplicity of the structure of polythene is to some extent misleading, and the effects produced by radiation are complicated by several factors which do not operate to the same extent in other polymers. In spite of the spate of published work in this field it is therefore not yet possible to give an unambiguous and quantitative answer to many fundamental questions. The main factors which complicate the issue, but which must be taken into account, are the presence of crystallinity, the unknown size and distribution of side chains, and the difficulty of assessing molecular weight distribution. A question of obvious importance is to discover whether crosslinking takes place equally well in the crystalline and in the amorphous regions of the polymer, and whether it is temperature dependent. These and other problems will undoubtedly be solved in the near future; that no answer to them is yet forthcoming is only due to the comparative newness of this subject. In spite of these tremendous gaps in our basic knowledge, sufficient data are already available to enable industrial development to proceed hand in hand with basic research. This is probably the most rapid means of extending our knowledge of this field.

GENERAL EFFECTS

When polythene is subjected to high energy radiation a number of changes are observed. Hydrogen gas is liberated together with paraffins such as methane, ethane, and propane in smaller amounts; the polymer becomes increasingly insoluble, and cannot be melted into a liquid; with increasing radiation dose it becomes yellow and eventually dark ruby in colour; at first it becomes more flexible and transparent but after protracted radiation it hardens and becomes brittle. There are notable changes in the infra-red and ultra-violet spectra, and if the irradiation takes place in air a wax-like soft surface layer may be formed.

These and other but less obvious changes may be largely explained in terms of the following fundamental changes due to radiation:—

(1) Hydrogen is evolved and C–C bonds are formed between molecules. These bonds transform the polymer from a thermoplastic to a thermoset material. This is by far the most important change, known as crosslinking, and gives the process its industrial importance.

(2) At the same time there is an increase in unsaturation which may be essentially the same process as (1) but occurring within the same molecule.

(3) Radiation also destroys crystallinity when polythene is irradiated in the solid; this reduces the forces holding the molecules together below the melting point, and produces a more flexible material.

(4) Surface oxidation takes place under the influence of radiation.

(5) The cause of the colour change is not yet clear but may be due to the formation of conjugated double bonds.

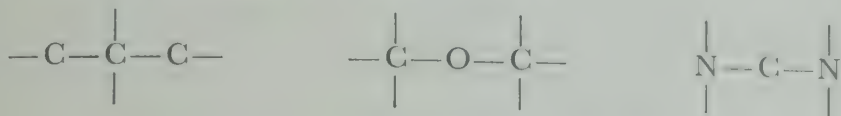
The effect of crosslinks on the physical properties of amorphous long chain polymers has been studied theoretically over a period of years by a number of authors, including Flory, Gee, Mark, Rehner, Stockmayer and Treloar. Further theoretical studies along the same lines have been made by Charlesby in a form more convenient for comparison with radiation-induced crosslinking. In comparing these theoretical predictions with polymers crosslinked by chemical means great difficulties have arisen in assessing the degree of crosslinking. Radiation presents an admirable means of inducing crosslinking in a quantitative manner and therefore enables one to confront these theories with experimental data. It says much for accuracy of these theoretical investigations that, where applicable, they represent to a remarkable degree of accuracy many of the properties of these irradiated polymers. However these theories are based on the assumption of flexible long chains and do not apply to polythene well below its melting point where crystallinity serves to immobilize the chains. They are however found to be valid above the melting point, or in the swollen state, when crystallinity has been eliminated.

THE TRANSITION FROM THERMOPLASTIC TO THERMOSET MATERIAL

In a thermoplastic polymer the individual molecules, of high molecular weight, are present either in the form of linear or of branched molecules. The polymer retains its solid properties due either to the entanglement of these molecules, which below a certain temperature are relatively rigid and cannot deform (as in polystyrene), or alternatively to the presence of crystalline regions (as in polythene or in nylon) where the molecules lie parallel to one another and are held in position by weak secondary (Van der Waals) forces or possibly hydrogen bonds. As the temperature is raised the molecules acquire flexibility, or the crystalline regions melt, and the polymer is transformed to a viscous fluid. On cooling it sets again to any new shape, as would be the case for the solid-

ification of a crystalline solid such as a metal. This process of melting, flow, and solidification can take place repeatedly with no change in the molecular properties of the polymer.

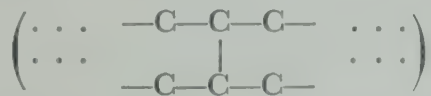
The physical properties of thermoset materials arise from very different causes. In the course of curing the original units become linked together not in a one-dimensional array but in a three-dimensional network by primary bonds, giving rise to groupings such as



Phenol formaldehyde resin is an example of this thermoset type of structure. The three-dimensional network is of an irregular type; diamond may indeed be considered as a polymer of regular network structure, but unfortunately we do not know how to polymerize it from its monomeric constituent!

The basic difference between thermoplastic and thermoset polymers is therefore the existence in the latter of a three-dimensional network held together by strong primary chemical bonds which once fractured cannot be reformed by simple thermal treatment. In breaking a piece of phenolic we physically fracture such bonds permanently. By irradiating polythene primary bonds are produced between molecules which were initially separable by gentle heating, sufficient only to overcome the weak secondary bonds between molecules. The bonds created by radiation are primary C-C bonds, as strong as those present in the initial molecules, and capable of being destroyed only at temperatures sufficient to decompose the material.

At which density of crosslinking does one find a transition from thermoplastic to thermoset polymer? This problem has been solved theoretically by Flory¹ for the case where all molecules are initially of the same size; Flory has also given a general solution as has Charlesby² who discusses the case where the initial molecular sizes follow any arbitrary distribution curve. In the latter case it is necessary to consider a "weight average" molecule, i.e. a molecule equal in weight to the "weight average" of the initial material as determined e.g. by light scattering. The transition from a thermoplastic to a partially thermoset material can be shown to depend on the average number of crosslinked units per weight average molecule (termed the crosslinking coefficient and represented by δ). The number of crosslinks per weight average molecule is $\delta/2$ since there are two crosslinked units per crosslink, e.g.:



The density of crosslinking, and hence δ , is proportional to the radiation dose R . For low values of R , when $\delta < 1$, crosslinking only results in

tying some of the original molecules together in twos, threes, etc. There is an increase in molecular weight and degree of branching, but the polymer is still thermoplastic, is still soluble and the melting point is unchanged. At the radiation dose corresponding to $\delta = 1$ a very small amount of a three-dimensional network appears. This is the gel point and forms the transition point from a fully thermoplastic polymer to one which is in part thermoset. As δ increases beyond 1 with increasing radiation dose, the network structure forms a rapidly increasing percentage of the total. The irradiated material can then be considered as consisting of two constituents—a sol and a gel fraction. The molecules not tied into the three-dimensional network are still soluble and form the sol fraction; the network itself is known as the gel and constitutes a three-dimensional molecule of very high molecular weight. There is therefore no sudden transition from thermoplastic to thermoset polymer. Rather is it a case of the polymer remaining completely thermoplastic up to a certain radiation dose, and then becoming partly thermoplastic and partly thermoset. In the literature the thermoset constituent is almost exclusively referred to as the gel; the distinction in terminology is of historical origin but may have a practical value, since the gel formed in this way is generally a much looser structure than is customary for the usual thermoset resins. By increased radiation alone a very firm and highly linked gel can however be obtained, and in this case the distinction between gel and thermoset loses its meaning as far as the final network structure is concerned.

SOLUBILITY

The shape of the sol fraction/ δ curve depends on the initial molecular weight distribution.² The initial slope of the curve depends on the ratio of the z average molecular weight (M_z), obtained e.g. by ultracentrifuge methods, to the weight average M_w . The first differential of the slope gives M_{z+1}/M_z etc. In general $M_{z+a} = \Sigma n M^{3+a} / \Sigma n M^{2+a}$ where n is the number of molecules of weight M . It is therefore possible purely from the shape of the curve to determine all the moments $\Sigma n M$, $\Sigma n M^2$, $\Sigma n M^3$, $\Sigma n M^4$. . . of the molecular weight distribution. To deduce the complete molecular weight distribution it is however necessary to know Σn , the number of molecules. This depends on the number average molecular weight which is not related to the shape of the solubility curve and must therefore be obtained by some independent measurement. Once the complete set of these moments is obtained the molecular weight distribution may be derived mathematically.

Baskett³ has presented an alternative technique for calculating these distributions from the sol fraction curves. The low molecular weight tails are not, of course, exactly defined and Σn can be estimated only by assuming reasonable functions for the extrapolation of this part of the distribution curve.

Crosslinking of polymers by radiation is usually ascribed to fracture of the side-chain (C-H in polythene) giving rise to a radical which can

link laterally on to another molecule. The alternative process of main-chain fracture by radiation leads to a rapid reduction in average molecular weight (degradation). Where the two phenomena (main-chain and side-chain fracture) occur simultaneously in the same polymer—side-chain fracture predominating—gel formation still results, but whereas in polymers suffering exclusively side-chain fracture and cross-linking the sol fraction rapidly tends to zero with increasing radiation alone, in the composite case the ratio of sol to gel tends to a limit depending on the ratio of side to main chain fracture.⁴ For polythene the sol/radiation curve follows this pattern with a ratio of fracture to cross-linking of about 0.35. For a similar ethylene polymer of lower molecular weight, the ratio is about 0.3. More direct evidence to the same effect has been produced by Baskett,⁵ and gives a somewhat lower ratio. This means that however prolonged the radiation dose a small fraction (6–10 %) of the irradiated polymer will still be soluble, though in practice it may be difficult to remove it from the crosslinked network. Once this sol fraction has been dissolved away, the remainder is entirely gel and is completely insoluble for an indefinite period.

SWELLING

Although irradiated polythene is insoluble in all the usual organic solvents (apart from the sol fraction) it will swell in them to an extent which depends on the density of crosslinks, and on the degree of interaction between solvent and polymer, usually defined in terms of a parameter μ . The theory of swelling which has been worked out by Flory and Rehner⁶ is based on the equilibrium between the elastic properties of the swollen network and the energy of dilution of the polymer by the solvent.

This theory leads to the following equation

$$\ln \left(1 - \frac{1}{V} \right) + \frac{1}{V} + \frac{\mu}{V^2} + \frac{\rho v}{M_c} \left(\frac{1}{V^{\frac{1}{3}}} - \frac{1}{2V} \right) = 0$$

where V is the volume ratio of swollen polymer (polymer + solvent) to that of the dry polymer, ρ is the polymer density and v is the molar volume of the solvent. M_c is the average molecular weight between crosslinks and within wide limits is therefore inversely proportional to the density of crosslinks.

Under suitable conditions, this equation can be simplified:

$$V^{\frac{2}{3}} = \frac{(0.5 - \mu) M_c}{\rho v}$$

Let R_g represent the radiation dose needed to reach the gel point i.e. one crosslinked unit per molecule of weight M_w . Then for a higher

radiation dose R , and a specimen of total atomic weight W there will

$$\frac{R}{R_g} \cdot \frac{W}{M_w}$$

crosslinked units and

$$M_c = \frac{W}{\frac{R}{R_g} \cdot \frac{W}{M_w}} = \frac{R_g M_w}{R}$$

Thus

$$V^{\frac{5}{3}} = \frac{0.5 - \mu}{\rho v} \cdot \frac{R_g M_w}{R}$$

A log-log plot of V against R should therefore give a straight line of slope $-3/5$. The coefficient

$$\frac{0.5 - \mu}{\rho v} \cdot R_g M_w$$

does not vary appreciably with molecular weight if the energy per cross-link does not so depend. Experiments on a number of polymers including paraffins indicate that this assumption is correct. Fig. 13.1 shows results for a high and a low molecular weight polythene. It is seen that

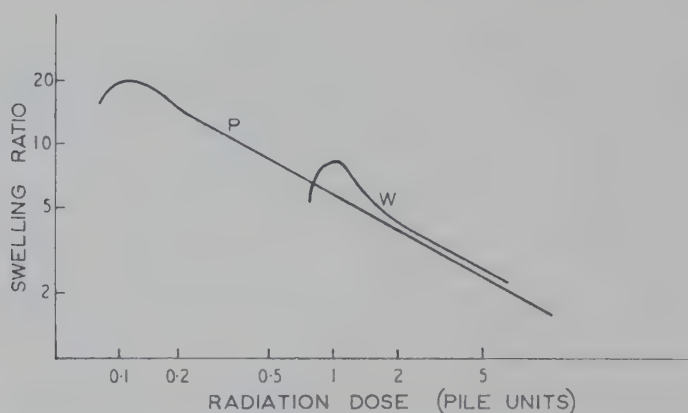


Fig. 13.1. Swelling ratio of crosslinked polythene (P) and low molecular weight ethylene polymer (W)

the same straight line of slope $-3/5$ represents correctly the experimental data over a wide range of radiation doses. For very high densities of crosslinking the simplified equation above fails to apply. For very low radiation doses, not greatly exceeding about $\delta = 2$, it also fails since in the simplified equation, no allowance has been made for end effects, the existence of a finite amount of sol (which cannot swell) and the difference between crosslinking density in sol and gel. To make quantitative corrections for these effects requires *inter alia* detailed knowledge of the

molecular weight distribution, but with plausible assumptions for this a reasonable approximation to the initial rising shape of the swelling curve may be deduced.

In other solvents, or at lower temperatures the swelling ratio may be considerably smaller. Nevertheless with many oils it is necessary to resort to very high radiation doses to keep the swollen volume to within 10% of its dry value.

FUSION

In ordinary polythene, the molecules are held together by the crystalline regions. As the temperature is raised the smaller crystals melt first, and the ratio of crystalline to amorphous material diminishes. At the melting point all crystals have melted and the polymer molecules are free to flow. At temperatures below the melting point the number of crystallites remaining is already inadequate to give good mechanical strength. For many purposes this imposes a serious limitation on the working temperature of the polymer.

Irradiation and the production of crosslinks does not increase the melting point of polythene, if by this is meant the temperature at which the crystalline regions melt. This can be seen in X-ray studies of the irradiated polymer, and also by a visual examination of the polymer at various temperature. The white wax-like appearance is due to the existence of spherulites and crystalline regions, and disappears fairly sharply at the melting point. In the irradiated specimens of polythene, the same effect is observed at the same or even at slightly lower temperatures. A more detailed comparison of the melting process in polythene (ordinary and irradiated) may be made by tracing the change in specific volume ($1/\text{density}$) as a function of temperature for a series of specimens irradiated to varying degrees. The experimental results may be represented graphically by curves as in Figs. 13.2 and 13.3. At 20°C the specific volume of 1.09 for unirradiated polythene comprises a fraction f of crystalline material of specific volume $V_c (= 1.00)$ and a fraction $(1 - f)$ of amorphous material of specific volume V_a . Because of the less dense structure of the amorphous regions $V_a > V_c$. Then at 20°C the specific volume of the unirradiated polymer

$$\begin{aligned} V &= 1.09 = f V_c + (1 - f) V_a \\ &= V_a - f(V_a - V_c) \end{aligned}$$

As the temperature rises, V increases rapidly in the manner shown in Fig. 13.2 to a value of about 1.25 at 115°C and then increases linearly with temperature beyond this point. The rapid rise below 115°C is due in part to the usual temperature expansion of V_c and V_a but is mainly due to the decrease in the crystalline fraction f from about two thirds at 20°C to zero at 115°C. There appears to be no fundamental difference between the amorphous regions and liquid polythene at the same temperature, except that the amorphous regions are limited and held in position

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by neighbouring crystalline regions. The uniform expansion rate above the melting point corresponds to the usual expansion of a liquid, and if extended below this temperature would represent the specific volume of the amorphous regions.

The shape of the curve for irradiated polythene is modified by two factors: the decrease in the degree of crystallinity and the presence of crosslinks which, particularly in the amorphous region, tend to draw molecules together. These two factors operate in opposite directions: the former increasing the total specific volume, the latter decreasing it. The net effect is shown in Fig. 13.3 for the irradiated polymers. Except for the most highly irradiated specimens there is little change in specific volume at 20°C but the subsequent increase at higher temperature is

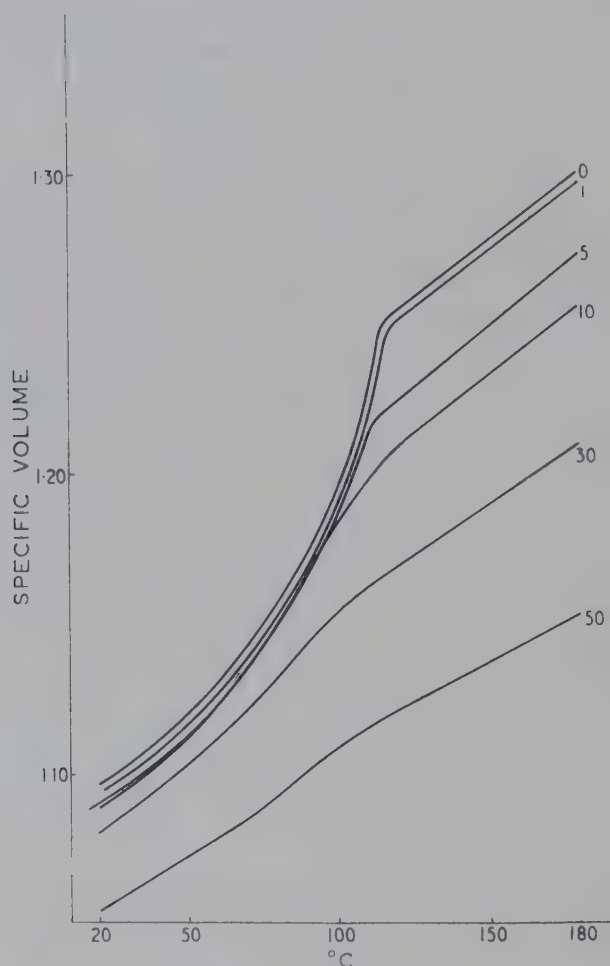


Fig. 13.2. Specific volume of irradiated polythene at various temperatures (Figures give radiation dose in pile units)

much smaller since there is less crystalline material available to melt and the specific volume of the amorphous regions is reduced by the presence of crosslinks. The point of inflexion which represents the temperature at which all crystalline regions have melted has not, however, been increased by radiation; in many instances there may be a decrease. Above this temperature the thermal expansion rate of the amorphous

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crosslinked material is lower and the polymer, instead of being present in the liquid state is transformed into a transparent, amorphous and elastic solid. The effect of radiation is not therefore to raise the melting point (in the sense of raising the temperature at which crystallinity disappears) but rather to change the material above its usual melting point from a viscous liquid to a rather elastic solid. The mechanical

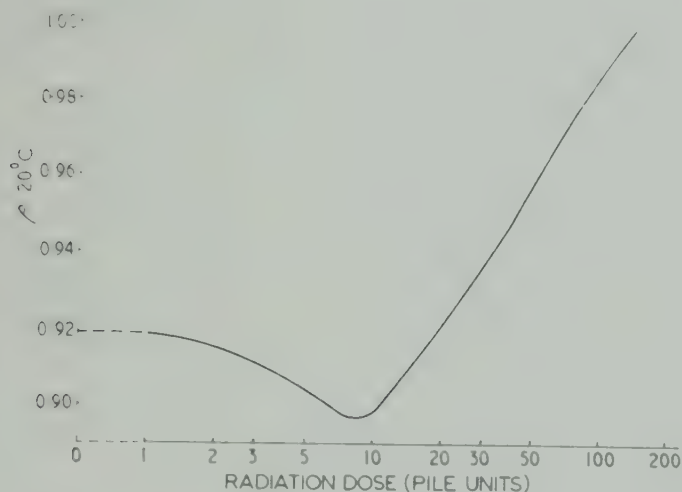


Fig. 13.3. Density of irradiated polythene at 20°C

properties of this solid will be discussed separately below. The temperature of irradiation is not unimportant. The higher it is (at least up to the melting point) the greater the degree of crosslinking and the subsequent reduction in crystallinity in the cold.

In highly irradiated polythene, all crystallinity has been destroyed even at room temperature. In this case, there is no evidence of a break in the curve and an approximately linear plot is obtained. The slope depends on the density of crosslinking, decreasing as further irradiation links the molecules more firmly together. It has indeed been possible to derive an approximate equation of state for such a crosslinked amorphous structure, which represents the variation of specific volume V with external pressure P , degree of crosslinking c and temperature T (°K). It is assumed that the expansion of primary C-C or C-H bonds or valency angles is unaffected by temperature, all expansion being due to lateral displacement of unlinked units. Then

$$(P + P_0) (V - V_0) = (1 - \beta(c)) RT/M$$

where P_0 , the internal pressure arises from the attraction (Van der Waals forces) of one element (C_2H_4) to another. V_0 is the minimum volume, when $T = 0$ and is approximately independent of degree of crosslinking. $\beta(c)$ is a function of the proportion of the units crosslinked and is close to c . R is the gas constant, and M the molecular weight (28) of the

unit C_2H_4 . This equation is somewhat reminiscent of the gas equation and indeed there are many useful analogies to be drawn between amorphous polymers and gaseous ensembles. The implications of this equation have been examined more fully in the literature.⁷

UNSATURATION

Although the most striking change which occurs when polythene is irradiated arises from the formation of crosslinks, other chemical changes are also produced—mainly increased unsaturation and oxidation.

The increase in main chain unsaturation $-C=C-$ is shown both by direct chemical titration with bromine vapour (Dole, Keeling and Rose⁸) or with Wijs solution (Black and Charlesby) and by infra-red evidence; in the latter case there is an increase in infra-red absorption at about 10.4μ , a wavelength which corresponds to *trans* unsaturation $RCH=CHR'$. No infra-red data on the *cis* unsaturation can be obtained.

Experiments with different forms of high energy radiation—namely electron beams, gamma rays and atomic pile radiation, reveal no essential difference in the production of unsaturation. Measurements on films and sheets of varying thickness show that the degree of unsaturation is independent of film thickness and occurs uniformly throughout the specimen. In this respect, radiation induced unsaturation is similar to crosslinking which is a volume effect, and differs from the oxidation effects which are largely dependent on the surface area and on external conditions during irradiation. Unsaturation of a similar extent is also produced when molecules with long aliphatic chains are irradiated and it would appear that this effect is a fundamental effect of radiation on long chain saturated molecules. Up to radiation doses of about 10 pile units or 500 megaröntgen, the increase in unsaturation is proportional to the radiation doses, but there is some tentative evidence that the unsaturation produced in this manner eventually reaches a maximum of about 1 double bond per twenty carbon atoms.

Estimates of the degree of crosslinking are closely bound up with these unsaturation measurements, since both crosslinking and unsaturation result in hydrogen evolution which can be measured. Existing estimates on unsaturation are, however, not very accurate so that one cannot deduce from them and from the hydrogen evolved, the number of crosslinks formed; the approximate data available indicate that unsaturation and crosslinking are of comparable amount. Unsaturation may indeed be considered as an alternative reaction to crosslinking but taking place between two adjacent carbon atoms within each molecule.

A further change which occurs on irradiation is the reduction of pendant methylene groups $RR'C=CH_2$ present in the original polymer. This reaction may be due to hydrogenation by the hydrogen evolved during radiation.

Oxidation during radiation appears to be largely a surface effect, and after high dosages results in a waxlike surface film which can be removed.

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Chapiro⁹ subjected 2 mm thick sheet of polythene to gamma radiation at room temperature in the presence of air and using tensile measurements as a guide to crosslinking density found that this depended on the intensity of the radiation as well as on the total dose. This dependence was ascribed to the penetration of oxygen molecules into the polymer network which then react with radicals to form carbonyl groups, whereas in the absence of oxygen, these radicals would form crosslinks. In addition, Chapiro suggests that thermally unstable oxygen bridges may also be formed in the polymer.

MECHANICAL PROPERTIES

The mechanical properties of unirradiated polythene depend largely on the presence of crystallites, which serve as extensive crosslinking regions; as the temperature is raised these crystalline regions progressively melt, and the polymer becomes more flexible; when all such crystalline regions have disappeared the polymer is transformed into a viscous liquid.

Radiation has two major effects on these mechanical properties; it produces permanent crosslinks between carbon atoms, and it reduces crystallinity. These two effects operate in different directions, the former increasing the stiffness (or elastic modulus), the latter reducing it. Since the degree of crystallinity is very temperature dependent, the results obtained by radiation can be very variable, depending on the dose and temperature of radiation, as well as on the temperature of measurement.

At room temperature, and for radiation doses of about 10 megaröntgen, there is an increase in the elongation at break and in the tensile strength. Both these effects are due to an effective increase in average molecular weight as molecules are linked together by radiation. Above this dose network formation begins and the elongation at break of the thermoset material formed is progressively reduced. Results published by Lawton, Balwit and Bueche¹⁰ for a low density polymer of molecular weight 21000 are given in the following table:

Radiation dose, megaröntgen	0	10	40	80	150
Tensile strength, lb/sq. in.	2,200	3,500	3,200	3,200	2,800
Elongation at break, %	580	750	380	220	100

At the same time as elongation at break is reduced there is an improved elastic recovery due to the rubberlike properties of the crosslinked network.

Radiation doses of between 100 and 500 megaröntgen have a considerable effect on the degree of crystallinity and at about this latter dose, crystallinity has almost disappeared, leaving a very flexible polymer with good elastic recovery. Apart from a yellow colouration which may be due to conjugated unsaturation, the polymer is then almost transparent and its mechanical behaviour is that of an overvulcanized rubber.

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As the radiation dose is increased above 500 megaröntgen, irradiated polythene becomes stiffer and more brittle; the degree of crosslinking is being increased with no compensating reduction in the degree of crystallinity, which has almost vanished. The minimum in the elastic modulus radiation curve corresponds to the point at which the rate of increase in stiffness due to radiation-induced linkages equals the rate of loss of stiffness due to destruction of crystallinity (Fig. 13.4).

In the temperature range above the melting point when all the crystallites have melted, and ordinary polythene has been transformed to a liquid, radiation-induced linkages serve to hold the polymer molecules together and impart true rubber-like elastic properties. For good elastic properties low degrees of crosslinking (of the order of 1 % of the carbons) are necessary and the tensile properties are poor. As against a tensile strength

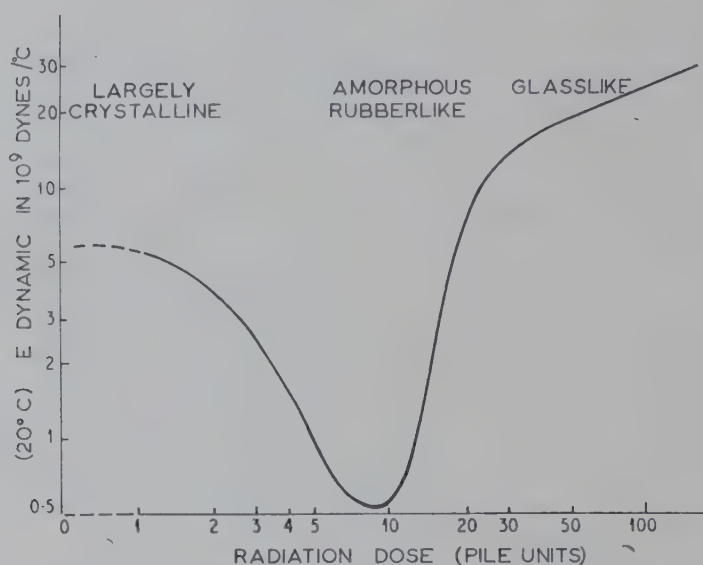


Fig. 13.4. Elastic behaviour of irradiated polythene at 20°C

at room temperature of about 2,200 lb/sq. in., the same polythene subjected to 15 megaröntgen only has tensile strengths of 430 lb/sq. in. at 105°C (when there is a residual amount of crystallinity) and 89 lb/sq. in. at 140°C. Higher radiation doses and higher initial molecular weights increase these values.

For another low density polythene, of average molecular weight 35,000, the corresponding figures are 510 and 155 lb/sq. in. at 15 megaröntgen, and 400 and 219 lb/sq. in. at 30 megaröntgen. The tension set at 105°C amounts to between 80 and 15 % while at 140°C it is zero, the crosslinked polymer then being a true rubber. These tensile strengths could be further increased by higher radiation doses, but only at the cost of ultimate elongation.

The theory of elastic deformation of rubber-like materials has been worked out on purely thermodynamic grounds, and gives an expression for the elastic modulus E of a crosslinked polymer in terms of the average

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molecular weight M_c between crosslinks. For small extensions, this may be written in a simplified form

$$E = 3\rho RT/M_c$$

where ρ is the density, R the gas constant and T the absolute temperature.

This theory can be readily applied to crosslinked polythene above the temperature at which crystallinity affects the elastic properties. Work along these lines has been carried out by Charlesby and Hancock¹¹ and by Lawton, Balwit and Bueche.¹⁰ The simplified expression given above does not take into account the presence of end groups due to the finite initial molecular weight, and entanglements between chains which may serve as crosslinks. Good agreement with experimental data has been found for radiation doses of up to about 20 units or 1,000 megareps. Beyond this point the elastic modulus increases far more rapidly than is indicated by the theory. This lack of agreement is not unexpected and arises from the high density of crosslinking (corresponding to these high radiation doses) which gives only short molecular chains between such crosslinks; these chains are too short to apply the statistical theory on which the treatment of rubberlike elasticity is based. The disagreement arises from the difference between rubberlike and brittle deformation.

Lawton, Balwit and Bueche have studied the shape of the stress/strain curve of polythene up to the breaking point. For high deformations

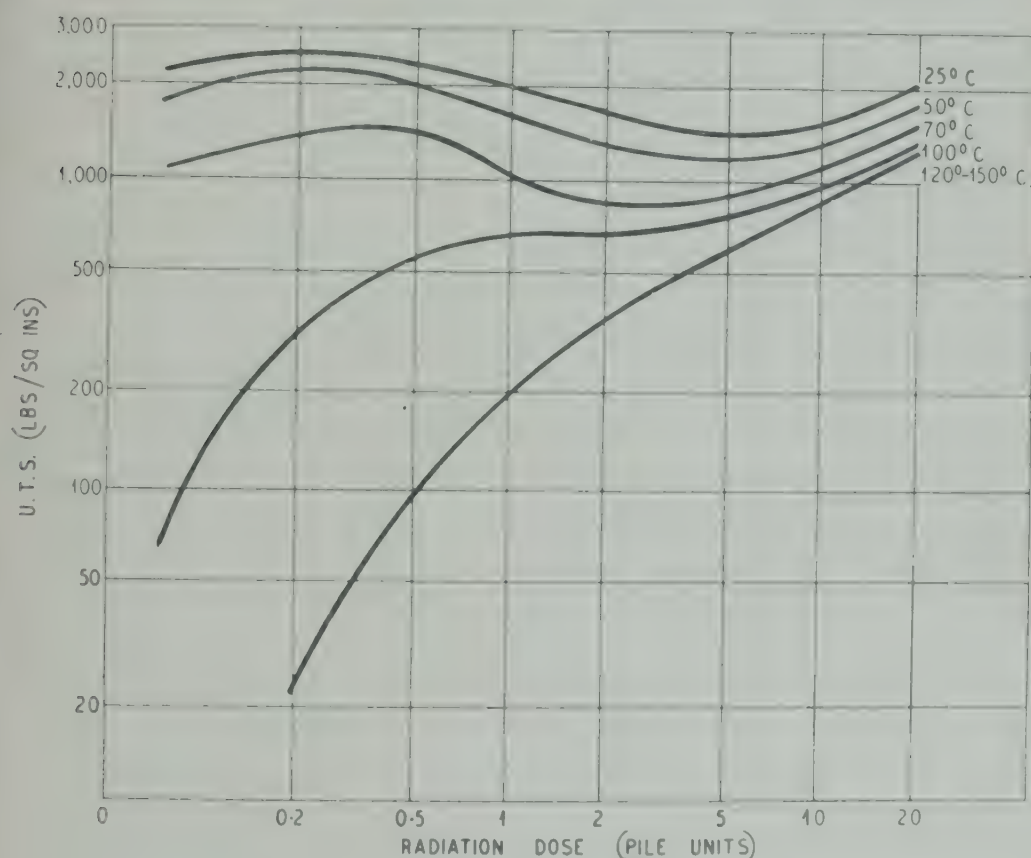


Fig. 13.5. Tensile strength of irradiated polythene

the stress is no longer proportional to the strain, but varies as the function $(\alpha - 1/\alpha^2)$ where α is the ratio of deformed to initial strength. Good agreement is found at temperatures above the usual melting point. Below this temperature elastic set, cold flow and the presence of crystallinity render any comparison useless.

It may be concluded that in the truly elastic region (i.e. above the melting point) quantitative agreement with theory is obtained for the elastic modulus; for the tensile strength no comparable theory is available. At temperatures below the melting point, as well as for very high radiation doses above it, no quantitative theory is available and only experimental data can be considered; these agree with the results which might be anticipated on general grounds.

Fig. 13.5 shows the ultimate tensile strength of polythene irradiated to varying extents and subsequently strained at various temperatures. It is seen that up to about 70°C there is no great improvement on the tensile strength due to radiation. At 100°C, a radiation dose of about 0.5 units is required to achieve about one quarter of the tensile at room temperature while at 120 or 150°C as much as 3.5 units is needed. It follows that crosslinking by radiation does not result in the production of a strong polythene above the usual melting point, the amount of radiation being generally too low to provide sufficient crosslinks. However, at these higher temperatures, the deformations produced by external stresses are elastic in character and therefore quite different in character from the cold flow which takes place in unirradiated material. The use of irradiated material at high temperatures should therefore be confined to applications in which the applied stresses are not very high, or when elastic deformation can be tolerated.

At the time of writing, little information has been published on the irradiation of the high density polythenes. Their higher degree of crystallinity, due to the much smaller number of side chains, raises the melting point close to the limit for infinite *n*. paraffin chains, i.e. 136–137°C. Near this temperature the high density polythenes soften, and above it they melt into viscous liquids. After irradiation their behaviour above this temperature is that of a rubber-like material similar to that obtained in the case of low density material after radiation. Even at room temperature there is an increase in tensile strength when small doses of irradiation (of the order of 10 megaröntgens) are received. This increase is comparable with that observed when low density polythene is irradiated and presumably arises from an increase in molecular weight.

The analysis of the gases evolved when polythene is irradiated is a useful method of studying the presence of side chains (Harlin *et al.*¹²). Although the radiation energy is absorbed at random (any electron in a molecule is likely to become detached) the chemical effect tends to become concentrated at certain chemical bonds. This is an example of the so-called "energy transfer" effect which is observed in many aspects of radiation chemistry. Its cause is not yet clear although one view is that, with the removal of an electron, other electrons in the same molecule

can move freely into the empty orbit (the molecule acting as a conductor) until an electron deficiency is left at a specific bond. In low density polythene this effect accounts for the considerable evolution of side chain fracture, even at very low doses. In high density polythene the almost complete absence of gases other than hydrogen is an indication of the linear character of the molecule.

INTERACTION OF HIGH ENERGY RADIATION WITH MATTER

Various forms of high energy radiation are available to promote cross-linking in high molecular weight polymers. These include corpuscular radiation (fast electrons, protons, fast neutrons, alpha particles, fast neutrons) and electromagnetic radiation (X-rays and gamma rays). These different forms of radiation interact with matter in very different ways, the common property being the high energy carried by each particle or photon, an energy which is usually of the order of a million electron volts or more. Crosslinking may indeed be produced by radiation of much lower energy, e.g. by X-rays or electrons of 10^5 ev or less, but practical considerations of low intensity or low penetration prove a serious handicap to their use at present.

Owing to the very wide range of masses involved, and the different types of reactions possible with the irradiated material, the penetration of the high energy radiations enumerated above differ very considerably. A 1 Mev gamma ray for example will travel about 14 cm in water per collision and will then lose on the average less than half its energy. A 1 Mev electron will produce ionization along its track, particularly towards its end, and its depth of penetration in water will only be about 0.4 cm. An alpha particle of the same energy will produce intense ionization along a very short track, 0.5 cm in air or a correspondingly smaller range in water. A fast proton of 1 Mev will have a range of about 2.3 cm in air. In all these types of radiation the loss of energy is primarily due to interaction with the orbital electrons, and as for most elements (except hydrogen) these equal about half the atomic weight, the rate of energy absorption is to a first approximation independent of the chemical constitution or structure of the irradiated material. In the case of fast neutrons the major cause of energy loss is by a scattering collision with the nucleus and here the rate of energy transfer depends on the ratio of masses. On an equal weight basis hydrogen is by far the most efficient absorber of fast neutron energy so that in this case chemical constitution plays a major role. In water or polythene a neutron of 1 Mev will travel several centimetres per collision and will lose most of its energy in a collision with a hydrogen atom, which can then be considered as a fast proton, produced within the material. It is therefore seen that in comparing the use of various types of radiation one must consider not only the cost of production of the high energy radiation, but likewise its penetration. To avoid wasting radiation it is advisable to match the penetration of the beam with the thickness of the specimen to be irradiated. Over a limited range this may often be achieved in

suitable instruments by altering the applied voltage. In other cases it may be necessary to alter the type of radiation.

The most usual radiation sources are gamma beams, electron beams and atomic pile radiation which consists of a mixture of radiations including gamma and fast and slow neutrons. Gamma radiation in the range 0.1 to 10 Mev loses energy mainly by Compton scattering which may be considered as a billiard-ball collision between the gamma photon (considered as a particle) and an orbital electron in which on the average 14,000 ev (for a 0.1 Mev gamma photon) to 6.84 Mev (for a 10 Mev gamma photon) is transferred to the electron, which is ejected from its parent atom. In this case, we may consider a gamma beam as producing the same net effect as an electron beam, except that, due to high penetration of the photon before the high energy electron is released, the net penetration is much greater. In the same way we can consider a fast neutron as serving primarily to produce a fast proton within the specimen.

The removal of an electron from an atom (by Compton scattering of a gamma photon) or the ejection of a hydrogen atom or ion (by collision with a fast neutron) may be expected to result in the residual molecule being left in a very chemically-reactive state. However, this is not the main cause of the observed changes such as crosslinking. The energy absorbed in a specimen of irradiated polythene divided by the number of crosslinks produced gives a value of about 20 ev. Since the average energy transfer per primary collision with a gamma photon or fast neutron of 1 Mev is about 500,000 ev, it is seen that each primary collision which liberates only one electron or proton nevertheless results in the formation of some 25,000 crosslinks. These result from the ionization and excitation produced directly or indirectly by the secondary electron or proton liberated in the primary collision with the original gamma photon or neutron.

As a fast electron moves through a solid its electric field reacts with the orbital electrons of neighbouring atoms and imparts energy to them. If this energy is sufficiently high an orbital electron may be removed from the field of its nucleus—a process known as ionization. Alternately the energy may suffice only to lift the electron to a higher energy level—a process known as excitation. An electron removed by ionization may in its turn pass through the solid producing further ionization and excitation.

Ionization and excitation also result when a fast proton moves through the solid. In this case, the larger mass (and hence slower speed at the same energy) of the proton will produce more intense ionization and excitation than an electron of the same energy. The path will however be much shorter.

Early radiation work on gases indicated that the average energy required to produce an ionization (and hence an electron separated from a charged molecule, termed an ion pair) varied but little with the type of high energy radiation or even with the gas. For air the energy absorbed per ion pair formed is about 34 ev for X-rays or gamma rays, fast

electrons or protons and is largely independent of the energy of the primary radiation. It is generally assumed, although there is no decisive proof, that the same energy is absorbed per ion pair as is also needed in liquids and in solids. We could, therefore, expect that if crosslinking is a consequence of ionization and excitation, the number of crosslinks produced in a specimen will depend primarily only on the total energy absorbed in it, and not on the type of radiation or its energy, or even on its rate of delivery. The distribution of these crosslinks may, however, depend on the radiation characteristics, such as the density of ionization (highest near the track of a fast proton). The extent to which the effects produced depend on the quality and type of radiation as well as on the total energy is a fundamental problem in radiobiology. All the evidence available to date indicates that for irradiated polymers, the effects produced depend only on the energy absorbed per gram, at least to the accuracy to which crosslinking can be measured. Experiments carried out on specimens of polythene irradiated with either gamma rays, fast electrons or atomic pile radiation confirm that the density of crosslinking does not depend on the type of radiation used. This means that results obtained with one type of radiation, most convenient for experimental purposes, can then be immediately applied to other sources of radiation, allowance being made for any temperature effect.

High energy radiation can be produced in a number of ways. Atomic piles produce a mixture of radiations which are normally absorbed in the surrounding shield, but which could be used for irradiating polymers if the reactor design permits. Moreover, the spent fuel rods after extraction from the pile are highly active and produce suitable radiation, which is, however, of rapidly decreasing intensity. Fission products present in these rods can be separated out chemically and the longer lived products used as radiation sources. An alternative source is radioactive cobalt, obtained by irradiating cobalt in atomic piles, but here the amount of radiation available is likely to be small, sufficient only for small scale work.

The radiation treatment of materials is not necessarily bound up with atomic energy: the former is concerned with changes in the electronic structure, the latter with changes in the nucleus. By using high voltage electrical equipment, it is possible to produce the reactions described here without involving any nuclear reactions whatsoever. The devices used must be capable of producing high voltages to achieve the necessary beam penetration, and relatively high power output to obtain a useful yield of irradiated product. At present high-powered equipment is available capable of producing several kilowatts of radiation energy and depositing it within a small specimen. To achieve the same total power output from radioisotopes would necessitate a source of several hundred thousand curies even if all the energy emitted could usefully be absorbed. To achieve the same energy deposition within a small specimen would require sources of several million curies of radioactive cobalt or caesium.

Various types of high power electrical sources are now being used for this work, including linear accelerators. Van de Graaf electrostatic

generators and resonant transformers. X-ray machines are also utilized although their power output in terms of radiation energy is much lower. The changes produced in polythene by radiation from these sources is identical with that produced by radiosotopes, and the choice between them will be largely based on consideration of economics and of experimental requirements. One may envisage considerable competition between these alternative methods of producing chemical changes by radiation.

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CHAPTER 14

MODIFIED POLYTHENE

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POLYTHENE is a high polymer member of the paraffin hydrocarbon family and, like other paraffins, it is relatively inert to chemical reaction. Many of its uses, such as liners for chemical equipment or containers for reagents, depend on this lack of chemical reactivity. The polymer is not soluble in any media at room temperature, but several hydrocarbon and chlorinated hydrocarbon solvents will dissolve it above 60°C.

Because of its chemical inertness, polythene is not subject to easy modification. Reactions which have been studied include thermal degradation, oxidation, halogenation and chlorosulphonation. Products from chlorination and chlorosulphonation have bright commercial prospects and are discussed extensively. Oxidation and thermal degradation reactions are of theoretical interest and have helped to establish polymer structure and mechanisms of polymer decomposition. In the commercial use of polythene, however, much emphasis is placed on suppression of these reactions.

THERMAL DEGRADATION

In the absence of oxygen, polythene is stable up to temperatures of about 290°C.¹ At higher temperatures there is a decrease in the molecular weight of the polymer resulting in lower molecular weight solid resins, greases and oils. Gaseous products are not formed rapidly until a temperature of 370°C is reached, and ethylene is only a minor component among the many resulting products. Over thirty compounds consisting of *n*-alkanes, *n*-alkenes, *n*-dienes and cyclic hydrocarbons were identified by mass spectrometer when polythene was pyrolyzed at 400°C.² When polythenes of different average molecular weights were degraded at temperatures over the range of 375 to 436°C in vacuum, it was observed that the energy of activation of chain cleavage decreases with decreasing chain length of the polymer.³

The bulk of the degradation products formed from pyrolysis of polythene at the lower temperatures in the absence of air have formulas which correspond closely to $(CH_2)_n$. At the higher temperatures, unsaturation in the products increases. Evidence of the type of unsaturation developed is available from infra-red spectra of the products. The intensity of absorption bands in the 800–1,000 cm^{-1} region increases markedly as the temperature increases, indicating the presence

of $\text{RCH} = \text{CH}_2$, $\text{RCH} = \text{CHR}'$ and $\text{RR}'\text{C} = \text{CH}_2$ unsaturation.

When polythene is pyrolyzed at 450°C under reduced pressures⁴ the average chain length of the pyrolysis products is a function of the pressure used, and the higher the pressure, the lower the molecular weight of the products. Under these conditions, double bonds are formed largely as a consequence of the rupture of the carbon-carbon chain. When cracking is carried out in the presence of a catalyst, however, greater unsaturation can be obtained without affecting the chain length. Nickel-on-kieselguhr, cobalt, platinum, alumina and silica are all active catalysts for this reaction.

It has been proposed¹ that the initial step in the oxygen-free degradation of polythene is the rupture of a few weak links in the polymer chain. These are probably present only in very low concentration and probably are adjacent to carbonyl or other oxygen-containing groups introduced by catalyst or impurities in the ethylene. The initiation of degradation is followed by a chain reaction in which points adjacent to branches in the polymer chain are attacked by the free radicals formed. This mechanism explains the presence of the three types of unsaturation observed in the products.

OXIDATION

The energy of activation for the degradation of polythene in the absence of oxygen is much greater than for normal high temperature oxidation.⁵ Since oxidation is the preferred reaction, oxygen-containing products can always be identified in the degradation products if even traces of oxygen have been allowed to contact the polymer. The oxidation reaction is postulated to progress by the initial formation of hydroperoxides, as with other hydrocarbons. After mild treatment the final oxygenated products are largely ketonic.⁶ It has been shown that the temperature coefficients of reaction rate and the energies of activation for the oxidation of polythene, Fisher-Tropsch wax and vulcanized natural rubber are roughly comparable.

Photocatalyzed oxidation of polythene gives products which according to infra-red absorption spectra contain ketones along with larger amounts of aldehydes and acids than are produced by thermal oxidation. Vinyl and internal unsaturation is also increased.^{6, 7} The major electrical loss effects observed in polythene after light-catalyzed oxidation are attributed to stable, oxygenated structures resulting from decomposition of peroxides and hydroperoxides. The power factor of a polythene increased tenfold (0.00035–0.0035) when the carbonyl oxygen was increased by 0.05%, or by one oxygen atom per 2,280 methylene groups.⁵

Various methods for the controlled oxidation of polythene have been studied.⁸ Heating molten polymer at $160\text{--}200^\circ\text{C}$ for several hours on a mixing mill in contact with air yields carboxylic acids with molecular weights similar to those of the starting material. Peroxide catalysts accelerate the oxidation. The high molecular weight acids are partially

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crosslinked, are insoluble in hot aromatic hydrocarbons, and have increased softening points (above 120°C). The products may contain from 0.1 to 0.5% by weight of combined oxygen.

Another oxidation procedure consists of heating the polymer with an oxidizing agent such as nitric acid in the liquid phase.⁸ When 35–85% aqueous nitric acid is used at temperatures between 70 and 130°C for several hours, the products are largely dicarboxylic acids. The molecular weights may vary from 250 to well above 1,000 depending on the conditions used. Small amounts of nitro groups are also introduced into the products.

Oxidation of polythene in carbon tetrachloride solution at 70–78°C can be effected with mixtures of ozone and oxygen.⁸ The products obtained are chiefly partially esterified hydroxydicarboxylic acids of molecular weight 100 to 2,000. Polythene containing carboxyl groups is of interest commercially because it can be dispersed easily in water to give stable emulsions.⁹

HALOGENATION

The substitution reactions of polythene with bromine, chlorine and fluorine have all been studied, but chlorination has received by far the most attention. Both Imperial Chemical Industries, Ltd. (Halotheene) and E.I. du Pont de Nemours & Co., have explored markets for chlorinated polythenes, but as yet no large applications have developed. A tremendous variety of potential products exists. The molecular weight and structure of the polythene chain, the amount of halogen substitution, and the technique by which the reaction is carried out all have a critical bearing on the ultimate properties of the polymer.

Chlorination

A number of techniques have been employed for the chlorination of polythene. The first reports¹⁰ describe experiments in which polythene dissolved or dispersed in carbon tetrachloride or acetic acid was treated with gaseous chlorine. The reaction was slow, particularly for the higher chlorine-containing products, so catalysts such as iodine, aluminium chloride or ferric chloride were added to increase the reaction rate. Even under these conditions several days were required to introduce 50% chlorine into the polymer.

By adjusting the temperature of the chlorination, it is possible to improve significantly the efficiency of the reaction.¹¹ The initial chlorine is introduced at or below 45°C, and after the reaction progresses to a point where the rate of gas uptake begins to fall off, the temperature is raised above 55°C.

Illumination of the reaction zone either by natural sunlight or by artificial light greatly increases the rate of chlorination.^{12, 13} The most effective light for catalysis is rich in green and yellow, and should have a wavelength below 4,785 Angstroms. Certain azo compounds are

reported to be as effective as light for accelerating the reaction.¹⁴ When carbon tetrachloride is used as the reaction medium, it is desirable to remove nearly all oxygen from the reaction vessel. Small quantities of oxygen catalyze the reaction, but larger quantities inhibit it, and the start of the chlorination is delayed until substantial quantities of chlorine have built up in the solution. If the concentration of dissolved chlorine is allowed to approach about 7 grams per 100 grams of solution, chlorination may proceed with violence. This is likely to occur only at reaction temperatures below 50°C.

Carbon tetrachloride solutions of polythene which are viscous (because of high molecular weight or high polymer concentration) often go through a gel stage during chlorination. Gelation can be prevented by addition of chloroform to the solvent along with proper temperature control.¹⁵

Suspension chlorination.—Water, acetic acid and cold carbon tetrachloride are all satisfactory media in which to chlorinate suspensions of polythene. When water is used, a temperature between 50–65°C is recommended until about 42% chlorine is introduced and then a temperature above 75°C until the reaction is completed.¹⁶ Below 50°C the reaction is excessively slow, and above 65°C agglomeration of the polymer is apt to occur until the higher chlorine range is reached. For efficient reaction the polythene should be finely divided, preferably less than 40 mesh, and a wetting agent should be added to facilitate forming and maintaining the suspension. At least 9 parts of water per part of polymer are required to form a proper suspension, but if the product is to contain greater than 45% chlorine, 25 to 30 parts of water per part of polymer are needed because the polymer swells and becomes difficult to agitate. Light or azo catalysis is necessary to establish satisfactory rates of reaction at atmospheric pressure, but no catalyst is needed when the reaction is carried out at a pressure of 100 lb/sq. in.

A further refinement of the suspension chlorination method is the direct chlorination of polythene latex.¹⁷ The reaction proceeds rapidly either at room temperature or at elevated temperatures. This technique provides a method of chlorinating mixtures of polythene with other polymers such as natural rubber which may be available in the latex form.

Other techniques have been disclosed. Polythene added to liquid chlorine dissolves while being chlorinated. The reaction must be carried out under pressure, and the chlorinated product may be isolated by reducing the pressure.^{18, 19} Polythene may also be chlorinated through the use of sulphuryl chloride,⁵ oxalyl chloride or phosgene.²⁰

Consistency of polymer versus chlorine content.—The first effect of chlorine substitution on polymer properties is a reduced tendency of the chains to crystallize with a resulting depression of the crystalline melting point and a reduction in softening temperature. Initially the chlorine atoms along the chain are too widely separated to have appreciable effect on the low temperature flexibility. Soft, rubbery products are obtained in the range of 25–40% chlorine. At the higher chlorine contents, while the products

are amorphous, they become increasingly stiff, and both brittleness temperatures and softening points rise. These effects are indicative of an increase in the second order transition temperature, but the change is not sharp, and exact values have not been assigned.²¹ By chlorination of polythene a host of graded thermoplastics are available from soft, pliable elastomers to rigid, transparent plastics resembling unplasticized polyvinyl chloride.

Indications of chemical structure.—The method of chlorination is important in determining the structures and properties of the chlorinated product. In solution, the polythene molecule is usually in an extended form. In the early stages of reaction, the chlorination is probably fairly random since all the hydrogen atoms have about the same opportunity of being replaced. The effect of the greater reactivity of tertiary hydrogens is minimized by their very low concentration. As the reaction progresses, the randomness disappears, and certain preferred structures appear.

Infra-red analysis of the products indicates the distribution of chlorine in them.^{21, 22, 23, 24} At the lower chlorine contents, below about 35% chlorine, most of the substitution is for secondary hydrogen atoms, along with some primary and tertiary substitution. As the chlorine content increases, the $\text{—CCl}_2\text{—}$ groups (indicated by a band at 660 cm^{-1} found in the spectrum for polyvinylidene chloride) increase relative to the —CHCl— groups (indicated by a band at 620 cm^{-1} found in the spectrum for polyvinyl chloride) and the $\text{—CH}_2\text{—}$ groups ($1,460\text{ cm}^{-1}$). The band at $1,460\text{ cm}^{-1}$ disappears when about 65% chlorine has been introduced and when no undisturbed methylene groups ($\text{—CH}_2\text{—}$ without Cl attached to an adjacent carbon) remain in the polymer.

As the chlorine content increases there are gradual reductions in the intensities of the bands at $1,375\text{ cm}^{-1}$, associated with —CH_3 groups, and at 722 cm^{-1} , found in paraffins with more than four adjacent methylene groups. This latter band disappears altogether when the chlorine content exceeds 50%.

When polythene is chlorinated in suspension in cold carbon tetrachloride or in water, random substitution is not expected. Whether the polymer is swollen or not, it will still remain partly crystalline, and chlorination will be concentrated in the amorphous regions. In addition, since the suspended particles are agglomerates of many molecules, the molecules or portions of molecules near the surface will be more heavily chlorinated than those in the interior. Therefore, it is not surprising that at a given chlorine content suspension chlorinated polythene is more crystalline than solution chlorinated material. The X-ray pattern present in polythene at normal temperatures disappears from the solution chlorinated product at 35% chlorine, but not from the suspension chlorinated product until about 55% chlorine has been introduced.

Properties.—Chlorinated polythene prepared in suspension thus contains more crystallizable material resulting in greater hardnesses and higher softening points than exhibited by corresponding homogeneous

products. Suspension chlorinated polythene also contains portions molecules which are highly chlorinated. This structure reduces flexibility and increases the hardness through steric effects or interchange action. Table 14.1 compares the softening points measured by a needle penetration test (Vicat softening point with 1,000 g. load) of polymers containing increasing amounts of chlorine prepared by the two methods.

Table 14.1.—SOFTENING POINT AND CHLORINE CONTENT

% Chlorine	Softening point, °C	
	Solution process	Suspension process
0	90	90
8	69	79
28	below 20	65
40	below 20	69
50	40	77

Suspension chlorinated polythene is considerably less soluble than material prepared by the solution process. It is also stronger, harder and stiffer over a wide range of chlorine contents. It becomes self-extinguishing after 25% chlorine is introduced, whereas the solution chlorinated product requires nearly 40% to render it non-flammable.¹⁶ The effect of chlorine on the stiffness of the two products is shown in Fig. 14.1.^{16, 25} The tensile strength dependence on chlorine for the solution product is shown in Fig. 14.2. Comparable data for the suspension product are not available.

A method of obtaining a balance among the best properties of each product is available through the blending of solution chlorinated polythene of different chlorine analysis.²⁶ If the chlorine contents differ by more than about 10–15%, the resins are incompatible, and it is necessary to use three or more products in the blend.

Chlorinated polythene, like polyvinyl chloride and other chlorine-containing polymers, suffer loss of hydrogen chloride and degradation when exposed to high temperatures or ultra-violet light unless they are adequately stabilized. Treatment of the resin with propylene oxide results in improved heat stability.²⁷ Additional ingredients recommended for improved heat stability include glycidyl laurate and a metal deactivator,²⁸ or lead carbonate or other salts of lead, sodium or potassium which will neutralize hydrogen chloride.²⁹ For stabilization against ultra-violet light degradation, particularly for chlorinated polythene containing greater than 50% chlorine, the addition of phenyl salicylate or resorcinol dibenzoate is recommended.³⁰

Uses.—Compositions containing chlorinated polythene, fillers, plasticizers, stabilizers and other additives have been recommended for flooring compositions,³¹ electrical insulation³² and unsupported sheeting.³³

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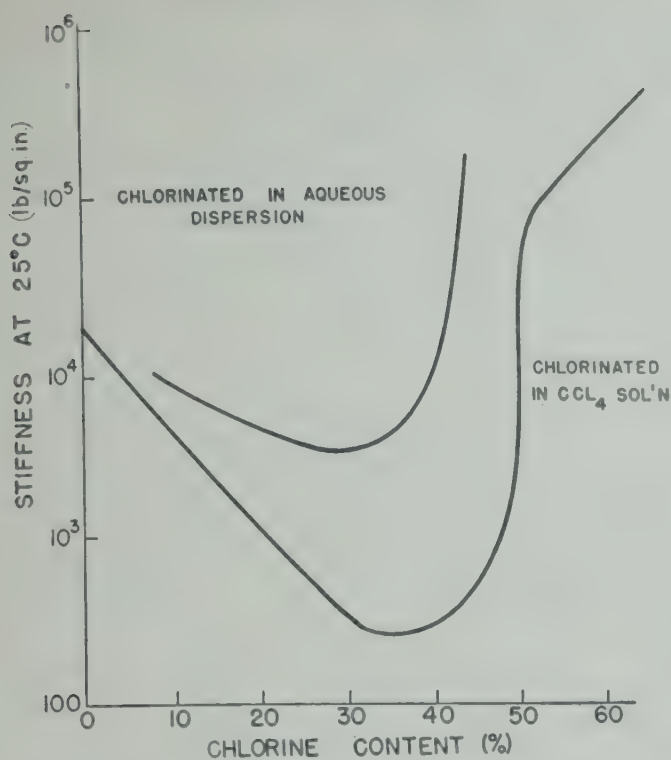


Fig. 14.1. Effect of chlorine on the stiffness of chlorinated polythene

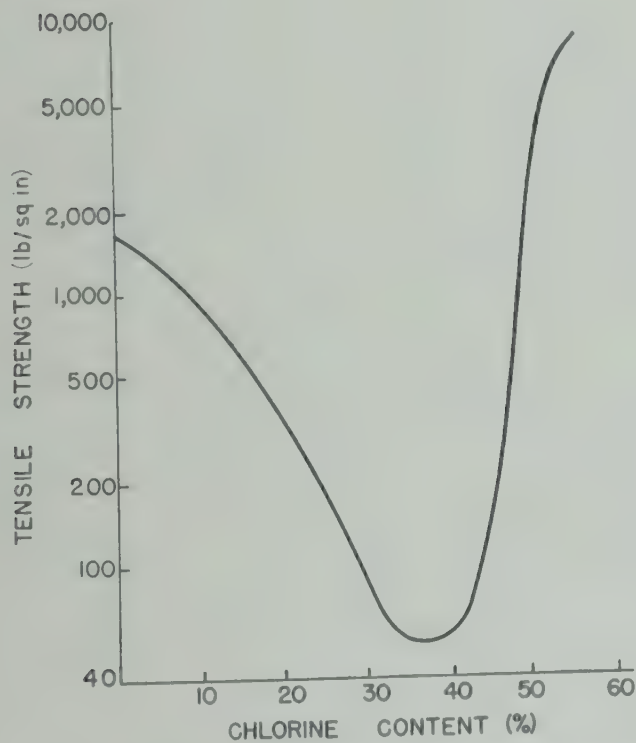


Fig. 14.2. Effect of chlorine on the tensile strength of polythene chlorinated in solution

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Certain metal oxides and salts and selected organic peroxy-compound can react with chlorinated polythene producing insoluble, less thermoplastic products.^{34, 35}

Shaped articles, particularly film, may be exposed to chlorine in gaseous or liquid systems to effect chlorination of thin surface layers. The increased surface polarity improves ink adhesion. A properly chlorinated surface will soften at a lower temperature than the polythene layer below it permitting films to be heat sealed with less loss of strength while at sealing temperature.^{36, 37}

Bromination

Polythene may be brominated quite readily. While steric factors must be a consideration, the relative amounts of chlorine and bromine substitution required to produce rubbery and rigid products tend to approximate the ratio of their atomic weights. Brominated polythene containing 55% bromine is rubbery, 71.5% is tough and 86% is hard and brittle.¹⁰

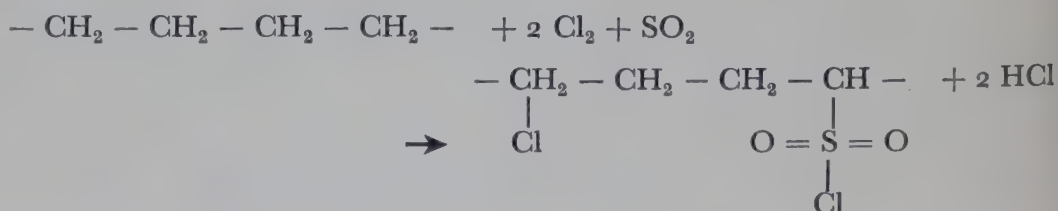
Fluorination

Polythene is fluorinated by treating thin film or powder with gaseous fluorine, while maintaining it in intimate contact with a non-reactive metal. Good contact with the metal must be maintained to prevent degradation, combustion or charring. Copper, nickel or phosphor bronze are satisfactory metals. Low temperatures (below 85°C) and fluorine diluted with nitrogen or hydrogen fluoride are necessary to prevent melting of the polymer and loss of surface area. Later in the reaction more stringent conditions can be used.

Polymers containing from 10 to 76% fluorine have been prepared. Fluorine at 76% represents the theoretical maximum, and this product resembles polytetrafluoroethylene. It has good electrical properties and excellent chemical stability; it is unaffected by boiling xylene or benzene and has a very high melting point. X-ray examination gives a diffraction pattern corresponding to polytetrafluoroethylene of very low crystallinity.³⁸

CHLOROSULPHONATION

When polythene is chlorinated in the presence of sulphur dioxide, various amounts of sulphonyl chloride groups may be introduced into the polymer.



Depending on the type of polythene used and the extent of chlorination and chlorosulphonation, a wide variety of products can be obtained.

A number of uses have been suggested which depend on the high reactivity of the sulphonyl chloride groups. Chlorosulphonated products of polythene of molecular weight 1,000 have been proposed for use as tanning and fat liquoring agents for leather and as intermediates in chemical synthesis.³⁹ The chlorosulphonated products of polythene having number average molecular weight values above 10,000 are rubber-like polymers which can be vulcanized.⁴⁰ Since these elastomeric polymers are completely saturated, they show a marked resistance to degradation by ozone, oxygen and other oxidizing agents.

Preparation of chlorosulphonated polymers

Many of the techniques for chlorosulphonation originally developed for lower molecular weight materials^{41, 42, 43} have been adapted to the chlorosulphonation of polythene.^{39, 40} Chlorosulphonation techniques in general resemble those of chlorination except that the presence of sulphur dioxide further restricts the choice of inert diluents. Similar catalysts are recommended.^{44, 45} Sulphur dioxide may be present during any part or all of the chlorination period. For most elastomer uses, homogeneous chlorosulphonation seems preferred (generally in carbon tetrachloride solution) in order to provide very pliable products, and polymers containing 20–45% chlorine and 1–2.5% sulphur are of widest interest. After reaction, solvent removal by steam distillation or by injection of polymer solution into a steam jet⁴⁶ has been suggested. The polymer can then be collected in the form of granular crumb-like particles which may be dried by any conventional method.

Polymers containing combined chlorine and sulphur dioxide are known to be lacking in stability, particularly when subjected to light or heat. Decomposition is often accompanied by darkening and the liberation of SO_2 and HCl . Stabilizers such as α - or β -pinene⁴⁷ and/or phenyl glycidyl ether⁴⁸ at concentrations of 0.1% to 1.0% are effective against degradation. Propylene oxide in conjunction with gelatin and octyl phenol has been suggested.²⁷ These stabilizers are most effective when added to the polymer in solution or to a water slurry of the polymer after its isolation from the synthesis medium.

An elastomeric chlorosulphonated polythene has been developed by du Pont, from polythene of about 20,000 number average molecular weight and is available under the trade-mark Hypalon chemical rubber. The white solid contains approximately 27.5% chlorine and 1.5% sulphur. Most of the chlorine is substituted along the hydrocarbon chain, approximately one chlorine atom for every six or seven carbon atoms. Some of the chlorine is combined with sulphur dioxide to form sulphonyl chloride (SO_2Cl) groups, which serve as the crosslinking sites, one for about every 100 carbon atoms.⁴⁹

Properties of uncured chlorosulphonated polythene

The uncured polymer is a somewhat tacky, rubber-like material of low tensile strength. Its density is 1.1. It is readily soluble in aromatic

and chlorinated hydrocarbons and, to some extent, in ketones, esters and alicyclic hydrocarbons. It is insoluble in acids, aliphatic hydrocarbons, alcohols and glycols.

The polymer has excellent resistance to ozone attack, but it is degraded by exposure to ultra-violet light unless protected by pigments or other compounding ingredients. Prolonged heating at 120°C or above will result in some decomposition with loss of sulphur dioxide. Although the polymer is not hygroscopic, contact with moisture may result in hydrolysis of the sulphonyl chloride groups, thus effecting a change in curing characteristics.

Unlike other elastomers, chlorosulphonated polythene does not show a large drop in melt viscosity with extended mastication. However, it is more thermoplastic than other elastomers and, therefore, becomes more plastic with increasing temperature.

Curing mechanisms

From the structure of chlorosulphonated polythene one would expect that crosslinking could occur through the following types of reactions⁵⁰:

- (1) Sulphonyl chloride groups, RSO_2Cl , can react with metal oxides to form salts, or with bifunctional amines to form sulphonamide groups, etc.
- (2) Chain chlorine atoms, particularly those on tertiary carbon atoms or adjacent to sulphonyl chloride groups, may react with diamines, dimercaptans, and other groups to eliminate HCl between the reactants and form bonds between the chains.
- (3) Olefinic groups formed by splitting out HCl or SO_2 and HCl may react with sulphur and rubber accelerators to form crosslinks, as in natural rubber cures.
- (4) Hydrogen atoms on the chains may be used in typical crosslinking reactions.

All of these mechanisms have been demonstrated by gelation tests.⁵¹ Commercial curing formulations may involve more than one of these reactions.

Vulcanizates of chlorosulphonated polythene can be obtained by curing with peroxy compounds such as benzoyl peroxide in amounts of 1% to 20%.⁵⁵ Quinone dioxime has been recommended as a crosslinking agent, particularly in the preparation of adhesives from chlorosulphonated polythene.⁵² Carbon black produced by the channel process appears to react with chlorosulphonated polythene, in the absence of any additional ingredients, to give products possessing good stress-strain properties.⁵³

However, most industrial formulas involve reactions with bi- or polyvalent metal oxides,⁵⁴ or with salts such as tri-basic lead maleate. Magnesium oxide produces vulcanizates of excellent properties except for water absorption. Litharge and tri-basic lead maleate produce equally good vulcanizates which are water resistant.⁵⁵ The crosslinking

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mechanism between a metal oxide and chlorosulphonated polythene is believed to be the reaction between the metal oxide and a sulphonic acid group on the polymer chain. The first step in the cure is then necessarily the hydrolysis of the sulphonyl chloride group to the free acid. The second step is the formation of a sulphonate bridge. These steps may be illustrated with a series of equations⁵⁶:



The sulphonyl chloride will not react directly with a metal oxide. The crosslinking reaction takes place at significant rates only under conditions where water is present, and the rate of hydrolysis of the sulphonyl chloride group to the sulphonic acid group is rapid. When all the ingredients in the formula are completely dry, or if a desiccant such as calcium oxide is added to the formula, little or no cure is obtained under normal curing conditions. On the other hand, the rate of cure is accelerated markedly by the addition of water to the formulation. For a safe processing composition, it has been recommended that the moisture content be maintained below 0.5% during processing prior to cure, and above 0.5% during cure.⁵⁷ Hydrated metal salts can be used to control moisture content.

A typical curing formula includes (per 100 parts of polymer) 10 to 50 parts of metal oxide, 2 to 10 parts of an organic acid, and 0.25 to 3 parts of an accelerator. Such a formula may be represented as follows:

Chlorosulphonated polythene	100
Magnesium oxide	20
Abietic acid (wood rosin)	2.5
Dipentamethylene thiuram tetrasulphide	1

Although the function of the organic acid is not known with certainty, it is believed to react with the metal oxide to solubilize the metallic ion and release water.



The water is then available for hydrolysis of the $\text{—SO}_2\text{Cl}$ groups.

The role played by the accelerators is not well defined. Certain of the accelerators, particularly those containing sulphur, have some curing activity when used alone in the polymer. A large number of accelerators are effective in chlorosulphonated polythene curing formulations. Among the typical rubber accelerators which have been most frequently used are mercaptobenzothiazole, benzothiazyl disulphide, and dipentamethylene thiuram tetrasulphide.

The compounded stocks may be cured by any of the conventional

techniques employed with natural and synthetic elastomers. Curing temperatures may range from 125°C to 160°C.

Other compounding ingredients

In addition to the ingredients necessary for curing, other common rubber compounding ingredients may be added to the chlorosulphonated polythene to enhance specific properties. These include fillers, softeners, extenders and antioxidants.

The tensile strength of vulcanizates at room temperature is not dependent on the reinforcing activity of fillers. Tensile strength values for unfilled stocks are as high as 3,500 lb/sq. in. At elevated temperatures, however, reinforcing fillers are needed for optimum strength.²⁵ Fillers are used to improve the processing characteristics of chlorosulphonated polythene, e.g., as by extrusion or calendering. Carbon blacks, whiting (CaCO_3), clay, barytes, blanc fixe, wood flour and calcium silicate have all been used successfully.⁴⁹ These materials increase the stiffness and hardness of the polymer and impair low temperature properties.

The addition of softeners or plasticizers to chlorosulphonated polythene compounds may be desirable for some uses, particularly those that require a Shore Durometer hardness of less than 60 on the A scale. Ester-type plasticizers, polyesters and petroleum hydrocarbons have been used. As a general rule, however, plasticizers should be avoided where maximum durability is desired because unplasticized stocks are usually superior in weathering, heat aging, tensile strength and resistance to abrasion.

Antioxidants generally are not necessary in compounding chlorosulphonated polythene. The complete chemical saturation offers excellent resistance to oxidizing agents. For maximum resistance to heat, however, an antioxidant such as polymerized trimethyldihydroquinoline is desirable.

Since chlorosulphonated polythene does not require carbon black to obtain good mechanical properties, it can be compounded in a wide range of colours. Coloured stocks show excellent durability in outdoor weathering.

Properties of vulcanizates

Cured chlorosulphonated polythene is unaffected by ozone and is highly resistant to degradation by oxygen or other oxidizing agents. Compared to other elastomers it possesses good tensile strength, is high in modulus and hardness, and low in elongation. The tear strength is comparable to that of other synthetic rubbers, but is less than that of black-reinforced natural rubber. The elastomer has unusual abrasion resistance, flex-life, and resistance to crack growth.

Although the cured polymer becomes stiff at low temperature, it is resistant to cracking upon impact flexing or in mandrel bend tests at temperatures as low as -70°C. At elevated temperatures the mechan-

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ical properties of the compounds are comparable with those of compounds based on other synthetic elastomers, but are inferior to those of natural rubber compounds. However, cured chlorosulphonated polythene is outstanding in retention of properties over long periods at high temperatures. It possesses good stability at 100°C in a wide variety of compounds. However, to obtain maximum stability at temperatures above 100°C, a mixture of magnesia and litharge is needed, and antioxidants are recommended. Fig. 14.3 shows the degree of heat resistance which may be obtained in a properly compounded stock. The curve shows the exposure time, at different temperatures, in which the ultimate elongation may be expected to drop from its original value to a value of 100%.

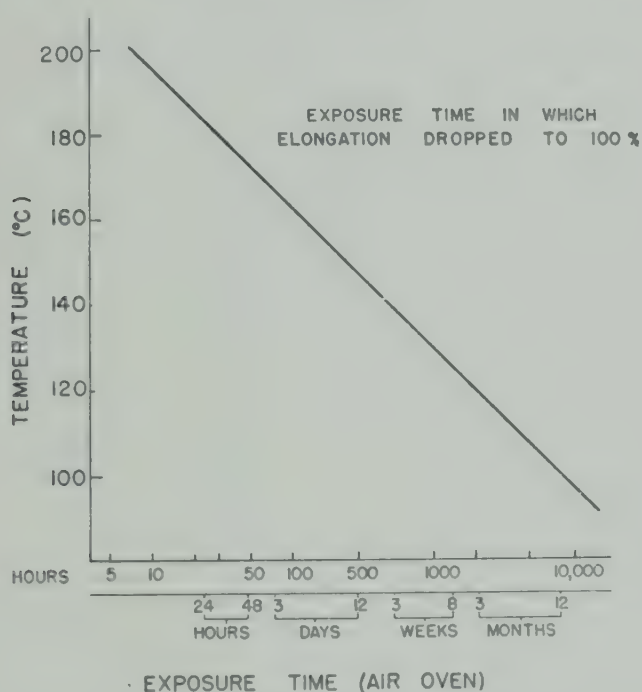


Fig. 14.3. Heat ageing characteristics of cured chlorosulphonated polythene

The vulcanizates possess good outdoor durability. Samples have been exposed for thirty months in Florida, U.S.A., with only minor changes in tensile strength, elongation and low temperature brittleness. Ultra-violet radiation, however, produces a crazing of the surface unless the stock has been protected by the incorporation of pigments with a high light-screening power.

The dielectric properties of chlorosulphonated polythene compounds are intermediate between those of natural rubber and neoprene; hence, they should be suitable for insulation at voltages up to 1,000 volts. Dielectric strength is good, and corona resistance is excellent.

Chlorosulphonated polythene compositions show an unusual degree of resistance to chemical attack, particularly by oxidizing agents such as sulphuric, nitric and chromic acids, chlorine dioxide and sodium hypochlorite. Dilute caustic, ethylene glycol and methanol have very little

effect. In resistance to mineral and vegetable oils the compounds excel natural rubber and butadiene-styrene copolymers, and approximate neoprene. Resistance to aromatic and chlorinated hydrocarbons is poor.

Applications

The durability of chlorosulphonated polythene compounds suggests a number of applications, many of which are practiced commercially. The new polymer may be used to provide ozone-resistant sponge weather stripping, and automobile window channels and ventilator strips. Leather-like coated fabrics in many colours have been made and appear to be ideal for heavy-duty applications, both indoors and outdoors.^{58, 59} Floor tile has been of interest because of good resistance to scuffing and indentation.³¹ Good corona resistance and heat ageing properties, together with a fair degree of oil resistance, have encouraged the use of the polymer in automotive products such as distributor boots, spark plug covers and ignition wire jacketing. High-pressure steam hose, industrial water hose covers, and brightly coloured garden hose have been made. Unusual chemical resistance has led to the production of industrial hose for the handling of corrosive chemicals, and to the lining of chemical tanks. Chlorosulphonated polythene has been used for surfacing fabric conveyor belts, particularly for conveying hot materials. White stocks make attractive conveyor belts for the food processing industry. The elastomer extrudes smoothly onto wire at good rates and can be cured in continuous vulcanization equipment to give products which are attractive for the wire and cable field, e.g., appliance cords, ignition wire, telephone handset cords, and weather-proof wire. The material has been used as gaskets or diaphragms where resistance to ozone, heat, oils or the weather is important. Chlorosulphonated polythene is used as an adhesive, either hot press or applied from solution.⁶⁰

One of the more important uses for this polymer is in the formulation of flexible, decorative and protective coatings in bright, stable colours for fabric, metal, rubber, masonry and other surfaces.⁶¹ The coatings may be prepared by dispersing or dissolving the ingredients of a complete curing formulation in a solvent such as toluene, and may be applied by brushing, dipping, spraying or spreading. Spreading doughs are made by dispersing the polymer in non-solvents such as methyl ethyl ketone and naphtha. Water dispersions have also been recommended for coating metal, chromic acid being added to improve the adhesion.⁶² Uncompounded, clear lacquers of chlorosulphonated polythene are applied to rubber goods to protect against ozone attack. These uncured coatings, however, are poor in tensile properties and abrasion resistance and, hence, do not last long in service. The elastomer has been recommended as a base for inks to be applied to wax-like plastics where ordinary inks will not suffice.⁶³

Blends with other elastomers.—Many of the desirable properties of chlorosulphonated polythene may be imparted to other elastomers by blending.

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Perhaps of greatest significance is the improvement in ozone resistance of unsaturated elastomers. This is illustrated for vulcanized Buna S-chlorosulphonated polythene blends in Table 14.2.

Table 14.2.—CONDITION AFTER 2 HOURS' EXPOSURE TO 135 PPM OZONE

Composition					
% Chlorosulphonated polythene	25	30	35	40	45
% GR-S 101 ^a	75	70	65	60	55
Extension of sample (%)					
20	U*	U	U	U	U
25	F**	U	U	U	U
40	F	U	U	U	U
50	—	F	U	U	U
75	—	—	F	U	U

*U = unchanged.

**F = failed by ozone cracking.

^a A typical Buna S (Styrene-butadiene Copolymer)

In addition, blending with chlorosulphonated polythene improves the oil and abrasion resistance of natural rubber compounds, the modulus and heat resistance of butyl rubber compounds⁶⁴ and provides plasticizer-free nitrile rubber compounds with good combinations of oil resistance and low temperature toughness. Care must be taken in compounding to insure that both elastomers can be cured properly. Buna S blends with their excellent abrasion resistance have been suggested for ozone-resistant military tyres, natural rubber blends for white sidewall tyres and coloured window channeling. A three-way blend with neoprene and natural rubber is used in white sidewalls on tyres. Blends with butyl rubber have been suggested for tyre curing bags, and blends with nitrile rubber for gaskets and diaphragms.

The impact strength of polyvinyl acetal resins may be increased five-fold or more by the addition of 5 to 10 parts of chlorosulphonated polythene.⁶⁵ The same type of improvement in impact strength has been obtained with polystyrene. In this case the chlorosulphonated polythene was dissolved in the styrene monomer prior to polymerization.⁶⁶

Derivatives of chlorosulphonated polythene

Derivatives of chlorosulphonated polythene have been prepared by allowing the polymer to react with monofunctional amines and alcohols.²⁴ Sulphonamide formation may be represented as follows:



The sulphonamides form cross links with diisocyanates or formaldehyde, whereas chlorosulphonated polythene itself does not. On the other hand, *p*-quinone dioxime, *p*-phenylenediamine, or ethylene diamine,

which form gels with chlorosulphonated polythene, have no effect on solutions of the sulphonamide derivatives. Various sulphonamide derivatives have been recommended as coating agents.^{67, 68}

Sulphonic esters may be prepared by allowing chlorosulphonated polythene to react with ethanol, phenol or cyclohexanol. A base is required to serve as catalyst and as acid acceptor for the HCl which is evolved. Triethylamine has been most effective in this capacity.

These derivatives, in a manner analogous to the parent polymer, can be crosslinked with polyvalent metal oxides such as litharge or magnesia, dioximes such as *p*-quinonedioxime, or diamines such as benzidine.

CONCLUSION

From the foregoing it can be seen that a large number and variety of products can be produced through chemical modification of polythene. Of all these, it appears that chlorosulphonated polythene is receiving the most commercial attention.

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PART II

PROCESSING TECHNIQUES

CHAPTER 15

EXTRUSION PROBLEMS AND SCREW DESIGN

A. KENNAWAY AND D. J. WEEKS

EXTRUSION of a plastics material is a process of forcing the molten material through a die to form a product of a specified shape. At one time this was done with a ram, but ram extrusion has the disadvantage that it is not easily made continuous. At present polythene is most often extruded continuously by feeding it in granular form to a screw or screws, where it is melted and forced through the die. In designing an extruder the screw is a major problem.

This chapter first describes two main types of extruder on the market at present. After considering the mechanical action of the screw, equations are given which describe approximately the screw action in single-screw machines when the extrudate is molten. The effect of these theoretical considerations on design is discussed at length together with an outline of the effects on performance of the various controls.

EXTRUDER TYPES

Extruders are usually classified by the number of screws used and their diameter. Plate 15.1 is a good example of a modern single screw extruder. The driving motor is mounted in the base close to the floor, and the drive is transmitted to the screw via belts and a reduction gearbox above the motor. Material is supplied through a hopper and feed pocket, which is a cut away portion of the barrel and is usually water jacketed. Plate 15.2 shows a screw for this machine. Screws of such machines can generally be cooled with water supplied and drained by pipes passing through the driving shaft in the gearbox.

Interesting features of the 2½ in. machine illustrated in Plate 15.1 are an infinitely variable gear giving screw speeds from 12 rev/min to 100 rev/min, a removable barrel section allowing the use of screws of different lengths, and barrel cooling if the stock overheats through mechanical working. The output is about 100 lb/hr.

Plates 15.3 and 15.4 show twin-screw extruders. The layout is generally the same as a single screw machine but the gearbox is necessarily more complicated, one of the main problems being to provide adequate bearings for the two screws which are close together. Twin-screw machines are on the market with screws rotating in the same direction, in opposite directions, meshing, and non meshing. The two screws

of the extruder shown in Plate 15.3 contra-rotate and intermesh. Each has three sections of different diameter. Electrical heating is used, and the screws are driven by a 10 horsepower motor at speeds from 6 rev/min to 18 rev/min, giving outputs in the region of 100 lb/hour.

Plate 15.4 shows another type of twin-screw machine with screws 90 mm diameter rotating in opposite directions. The screws are driven through a variable speed gear. Barrel heating is electrical, and air or water cooling may also be used on the barrel if necessary. A bleed is provided for removing moisture evolved during processing. The hopper contains a separate rotating screw which controls the feed to the screws in the barrel. Output is in the region of 200 lb/hour.

Filters are usually fitted between the delivery end of the screw or screws and the die of an extruder to exclude foreign matter from the product and to build up pressure. Filter and die design are dealt with elsewhere.*

Triple-screw extruders, and heated gear pumps fed from a melting device are occasionally used for extruding polythene.

Extruder barrels are heated either electrically or with fluids. Electrical heating seems to be increasingly popular as it is generally simpler to install. The advantages of fluid heating are that heat can be applied more uniformly and with lower local temperature than through electric elements, so hot spots can be more easily avoided; further a liquid system can absorb as well as supply heat and thus a cooling action is easier.

Thermocouples are usually fitted in the extruder barrel for temperature measurement. They can be made to operate heating controllers so that the barrel may be kept automatically at a predetermined temperature; however, these controllers are expensive. A cheaper type of on-off regulator is often used which can be pre-set to switch the heaters on for a fraction of a time interval and off for the rest of it. More complex types of barrel are available which can be heated electrically and cooled by fluids. By using a controller which can actuate both heating and cooling systems a preset temperature can be reached and maintained very rapidly.

For some purposes such as dispersing carbon black into polythene the mixing action of plain extruder screws is often not adequate, and extruders are now coming onto the market in which this disadvantage has been minimized. Twin-screw machines with kneading sections generally without flights along the screws are used so that the material is mixed as in the nip of a pair of rolls. A single-screw can be made a better mixer by attaching a kneading head to its front end. Longer screws are also frequently used.

Other recent developments are the provision of vacuum take-off points along the barrel for removing moisture evolved during processing and injection points for introducing pigments by stages during processing.

* See Chapter 16.

The more progressive machinery manufacturers supply a complete extrusion unit including take-off and wind-up gear.

OPERATION OF EXTRUDER SCREWS

Fig. 15.1 is a diagram of a single-screw extruder. The screw does three operations in order. These are: picking up the feed from the hopper; conveying the cold granular polythene while it is being melted, (which occurs at about 110°C for low density polythene, and about 130°C for high density polythene); compression and heating of the molten polythene, during which some homogenization occurs.

If there were no drag between the barrel wall and the material in the screw just inside the barrel, there would be no delivery as the granules

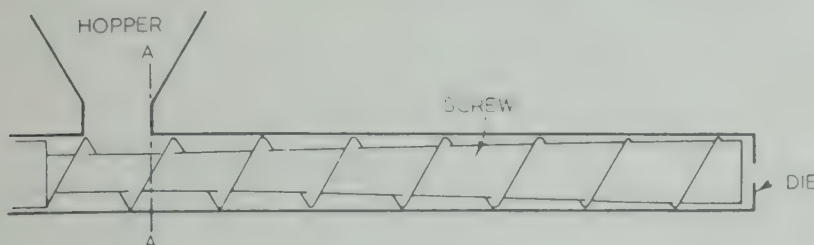


Fig. 15.1. Diagrammatic sketch of single screw extruder

would rotate with the screw. Conversely, maximum delivery of material would be expected if there were drag between the granules and the barrel but none between the granules and the screw. The action is then be akin to that of the fixed nut on a rotating screw, and if the other sections of the screw do not interfere the maximum delivery past the plane A-A (Fig. 15.1) per revolution is equal to the volume of one turn of the screw thread (or threads). In practice all surfaces exert drag on the granules and the sections upstream may restrict the feed. The volume delivered by the feed section as a percentage of the maximum possible is the feed section volumetric efficiency, which in practice is usually between 20 % and 40 %. The maximum attainable is about 50 % assuming equal friction on all surfaces.

The feed section volumetric efficiency is governed partly by geometric design of the feed hopper. Some granules fall into the screw against the direction of rotation, and the leading edge of the feed hole should be rounded to make this easy if high volumetric efficiency is wanted. The axial length of the feed hopper should be at least equal to the screw pitch. High bulk density and free flowing granules also help to increase the volumetric efficiency. However, screws in polythene extruders are usually designed at present so that the front end of the screw limits the throughput, and consequently high feed section volumetric efficiency is not of great importance.

The action of the screw inside the barrel is best illustrated by un-rolling the screw thread and barrel as in Fig. 15.2. The upper plate,

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representing the barrel, moves relative to the channel, representing the screw, in the direction shown by the arrow, and it tends to drag the material in the channel in this direction.

This drag can be resolved into components z and x parallel and normal to the channel. The component parallel to the channel tends to drag

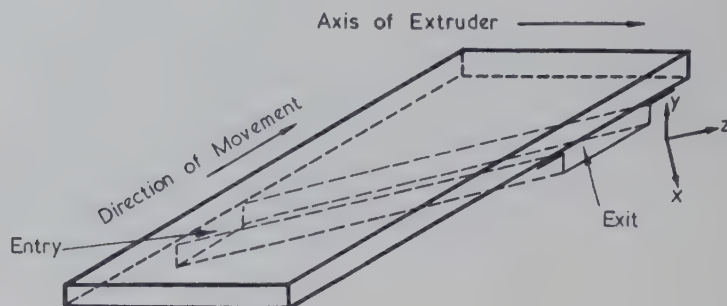


Fig. 15.2. Unrolled screw and barrel

material to the delivery end, and the normal component causes a rotation which is thought to be important for mixing the material and producing a homogenous melt. Other secondary flows are likely to be superimposed on these owing to leakage across the flights.

The specific heat of low density polythene is higher between 40°C and 105°C than above 120°C when the material is molten, and consequently for a final temperature of 200°C more than half of the total heat added is used in melting the polymer. Approximate calculation shows that it is unlikely that heat conducted from the barrel to the polymer could account for the melting by itself and some of the heating in this section is caused by mechanical working of the polymer by the screw. It is possible to run polythene extruders so that the heat generated in the material compensates for losses to the atmosphere and to cooling water;

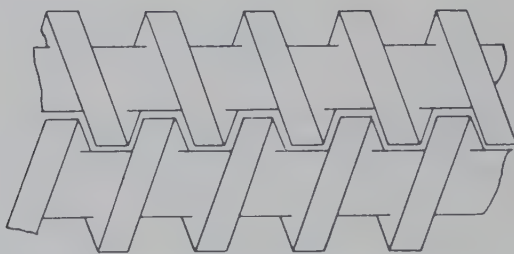


Fig. 15.3. Contra-rotating intermeshing screws

in this way no external heat need be applied. This is called "adiabatic" or more properly exothermic operation. Heating of the material by internal work as opposed to conduction is thought to produce a more uniformly melted product, though barrel heating is still necessary for starting up.

The foregoing considerations apply to single-screw extruders. In multiple-screw machines, the action is somewhat different. There are two main types of multiple-screw machine. In one type the screws intermesh, and the material when once fed into one screw is in a passage with ends at least partly closed by the flights of another screw (Fig. 15.3). This means that as a whole the material will travel in an axial direction except for leakage past the ends; the multiple-screw machine is more a positive pump, whereas the single-screw is a drag pump. This type of multiple-screw machine will in general have a greater pumping capacity than a single-screw machine of the same size running at the same speed but less shearing work will be done on the material, which means that more heat may have to be added externally and that homogenization

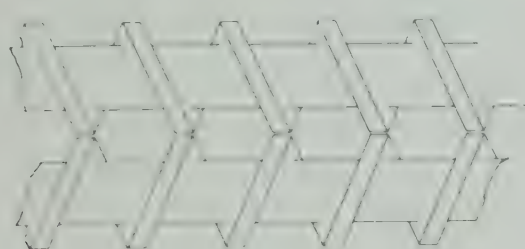


Fig. 15.4 *Contra-rotating unmeshed screws.*

may not be quite so good. These machines normally run more slowly than single-screw machines to allow time for melting.

In the other main type of twin-screw extruder the screws do not intermesh, as in Fig. 15.4. The action of the screws on the material appears to be a cross between positive pumping and drag pumping. With this type of machine homogenization may be quite good.

INTRODUCTION TO SCREW DESIGN

A good deal has been published on the analysis of flow in single screws, and attention will be confined to them here. No theoretical work seems to have been published on the design of multiple screws though the intermeshing type would probably yield to attack. What follows will apply to some extent to the non-intermeshing type.

Most single-screw extruders on the market at present are general purpose machines for making a variety of products from different materials and the screw design is dictated by the need for versatility. However, in this discussion it will be assumed that a screw is required specifically for extruding polythene.

The problem is to find the length and dimensions of the screw channel, the screw speed and power required to heat uniformly, homogenize and deliver a given quantity of material at a constant rate.

The next section is concerned with developing equations for Newtonian melt flow in single screws when no heating of the polythene is occurring.

The notation used in this section is as follows:

- b screw channel width.
- b_1 width at the point where the channel is filled with viscous liquid and $P = 0$.
- b_2 width at the delivery end of the screw.
- h screw channel depth.
- h_1 depth where the channel is filled with viscous liquid and $P = 0$.
- h_2 depth at the delivery end of the screw.
- g acceleration owing to gravity.
- w velocity component in the z -direction.
- y axis normal to the bottom of the screw channel.
- z axis along the screw channel.
- l distance along the channel from the filling point where $P = 0$.
- l_e distance from the filling point to delivery end.
- P pressure.
- P_e delivery pressure of the screw.
- Q flow rate (volume/unit time).
- S shearing stress.
- W relative velocity of screw and barrel
- μ viscosity
- $\tan \theta = \frac{b_1 - b}{l} \text{ or } \frac{h_1 - h}{l}$

The relation between shearing stress and rate of shear for "Newtonian" fluids in streamline flow is described by Newton's assumption that:

$$S = \frac{\mu}{g} \cdot \frac{\partial w}{\partial z}$$

Equations of the flow of such a fluid in an extruder channel were first given by Rowell and Finlayson.¹ They considered only the drag component acting along the channel which causes the fluid to be delivered. The differential equation governing the flow (Navier-Stokes equation) is:

$$\frac{\mu}{g} \cdot \frac{d^2 w}{dx^2} + \frac{\mu}{g} \cdot \frac{d^2 w}{dy^2} - \frac{dP}{dz} = 0 \quad (1)$$

The axes are as in Fig. 15.5 and dP/dz is the pressure gradient. This equation is a statement of the fact that in steady flow there is no acceleration, and the sum of the external forces on a small element is zero. It can be integrated for constant μ and dP/dz to give an expression for the flow.

If the channel had infinite width the equation would be:

$$\frac{\mu}{g} \cdot \frac{d^2 w}{dy^2} - \frac{dP}{dz} = 0 \quad (2)$$

Rowell and Finlayson showed that for channel width-height ratios of about 10 or more, Equation 2 is a satisfactory approximation to equation (1). As it is sufficient to illustrate general effects, only the simpler form given by Equation 2 will be used here. Integrating twice with

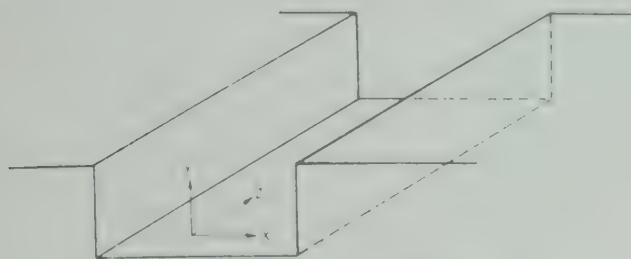


Fig. 15.5. Axes of reference

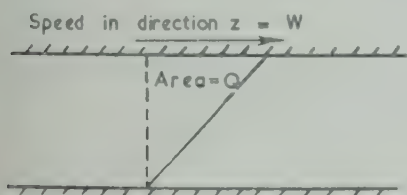
respect to y to obtain w , using boundary conditions $y = 0, w = 0, y = h, w = W$.

$$w = \frac{Wy}{h} + g \frac{(y^2 - yh)}{2\mu} \frac{dP}{dz} \quad (3)$$

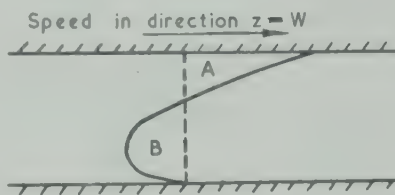
The flow Q in volume/unit time is given by $\int_0^h bw \, dy$. The integrated equation expressed in dimensionless form is:

$$\frac{Q}{Whh} = \frac{1}{2} - \frac{gh^2}{12\mu W} \frac{dP}{dz} \quad (4)$$

Any consistent set of units may be used.



$$\frac{dP}{dz} = 0, \quad \frac{Q}{Whh} = \frac{1}{2}$$



$$\frac{Q}{Whh} = 0, \quad \frac{h^2}{\mu W} \frac{dp}{dz} = 6$$

Fig. 15.6. Extreme velocity gradient profiles in a screw channel

Velocity gradients when $dP/dz = 0$ and when $Q = 0$ are given in Fig. 15.6. Leakage across the tops of the flights has been ignored. Equation 4 is plotted in Fig. 15.7.

Several workers^{1, 2} have made flow measurements on Newtonian or near-Newtonian fluids in extruder screws which substantiate the assumptions made in the theory providing the temperature rise of the liquid being extruded is small.

Suppose that a high delivery pressure is wanted at specified value of Q and W and channel dimensions bh . Then Q/Wbh is fixed, and Fig. 15.7 shows that dP/dz varies inversely with h^2 , so that for high delivery pressure it is an advantage to use a small h and large b . Also, if Q is to be reasonably independent of back pressure a small h should be used, because this makes $\frac{gh^2}{\mu W} \cdot \frac{dP}{dz}$ smaller and brings Q/Wbh closer to $\frac{1}{2}$. The closer Q/Wbh is to $\frac{1}{2}$ the smaller the percentage decrease in Q if, say dP/dz , is doubled, other conditions remaining the same.

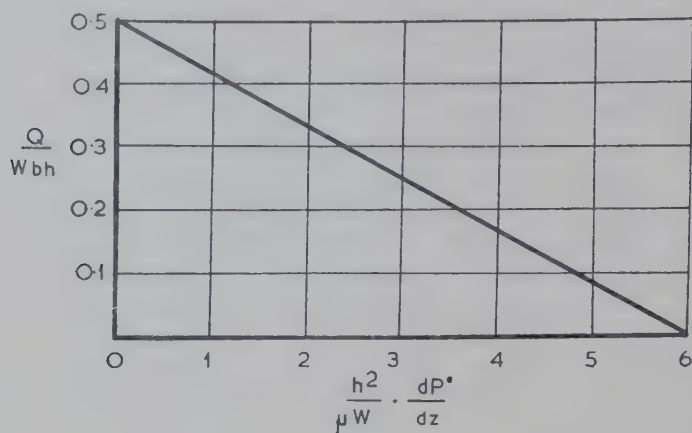


Fig. 15.7. Dimensionless plot of the simplified flow equation

Fig. 15.7 yields a further point of interest. For constant Q/Wbh , $\frac{gh^2}{\mu W} \cdot \frac{dP}{dz}$ is constant, and if heating of the fluid occurs with consequent decrease of viscosity the value of dP/dz must also decrease. Therefore in a screw of constant pitch and depth running at constant speed, the pressure gradient is proportional to the viscosity.

In a channel with uniform dimensions dP/dz is constant in Equation 4 and can be written as P_e/l_e . The relation between delivery pressure, length and output is given by:

$$\frac{1}{2} - \frac{Q}{Wbh} = \frac{gh^2}{12\mu W} \frac{P_e}{l_e} \quad (5)$$

With a full channel, if b decreases in the direction of flow, Q/Wbh will increase in the direction of flow. For constant μ the pressure gradient must then be greater at the beginning of the channel than at the end. If h decreases in the direction of flow, it can be shown that dP/dz increases when $Q/Wbh < 1/3$ and decreases when $Q/Wbh > 1/3$. If the flow is such that Q/Wbh is $\frac{1}{2}$ at a point in the tapering channel, the pressure will be a maximum here and will decrease either side. Thus beyond this point in the delivery direction Q/Wbh is greater than $\frac{1}{2}$ and the material is not being pumped by the drag of the screw alone but is being pushed from behind as well.

The connection between pressure and channel width in a screw with linearly decreasing pitch can be found by changing the variable in Equation 4 from z to x with the relation:

$$\frac{dz}{dx} = -\frac{1}{\tan \theta}$$

Integration of 4 between the limits $x = b_1, P = 0$ and $x = b_2, P = P_e$ gives

$$\frac{1}{2} \cdot \left(\frac{b_1}{b_2} - 1 \right) - \frac{Q}{Wbh} \cdot \ln \cdot \frac{b_1}{b_2} = \frac{gh^2 P_e}{12\mu Wb_2} \tan \theta \quad (6)$$

For linearly decreasing depth and constant width it can be shown similarly that:

$$1 - \left(\frac{h_2}{h_1} \right) - \frac{Q}{Wbh_2} \left(1 - \frac{h_2^2}{h_1^2} \right) = \frac{gh_2 P_e \tan \theta}{6\mu W} \quad (7)$$

The similarity between the flow of polythene and Newtonian flow will determine whether or not this treatment can be applied to molten polythene. It has been found experimentally that the shear stress—shear rate relation of low density polythene can be expressed by:

$$S = c \left(\frac{dw}{dz} \right)^n \quad (8)$$

with values of n ranging from about 1.4 to 2.5. It is possible to use this relation and obtain equations for the flow of polythene similar to the above. However, there are two difficulties. The constant c does not have the dimensions of viscosity unless $n = 1$, and in fact the dimensions of c depend on n , so that polythenes do not possess a viscosity in the accepted sense. Also the constants of the flow equation derived with this law are somewhat complex, making it difficult to apply. Since the flow equation is only a guide to performance in practice, the additional complication of allowing for deviation of polythene flow from the Newtonian does not at the moment seem justified, and it should be sufficient to use the apparent viscosities as given in Fig. 15.11.

APPLICATION OF THE MELT EQUATION TO GRANULE FED EXTRUDERS

Having discussed what happens in the feed and melting sections of a screw and outlined a simple flow theory where the material is molten, it remains to be seen what happens when they are all married in a working unit.

Broadly, screws can operate in two ways, which will be termed "unrestricted" and "restricted". A screw is unrestricted if it will deliver all that the feed section can introduce, and the screw output is then

POLYTHENE

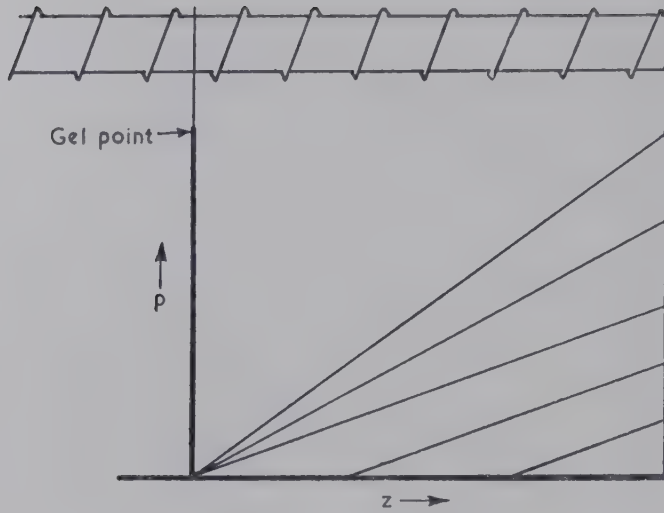


Fig. 15.8a. Constant pitch and depth screw. $Q/Wbh < \frac{1}{2}$

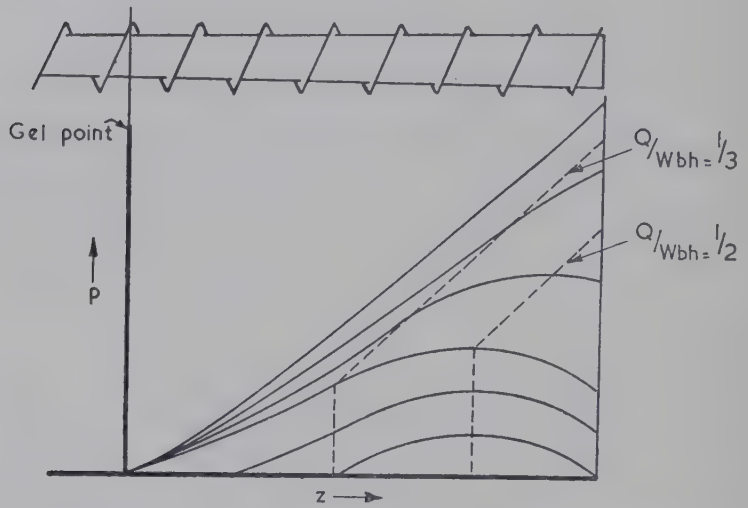


Fig. 15.8b. Decreasing depth screw. Unrestricted and $Q/Wbh_2 > \frac{1}{2}$, at low delivery pressure

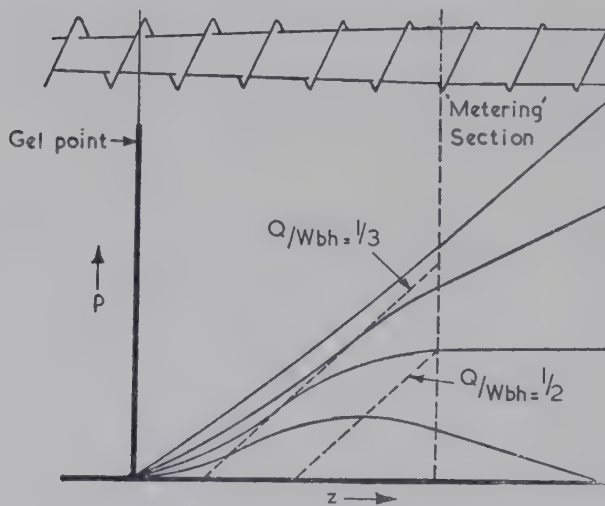


Fig. 15.8c. Decreasing depth screw with a metering section. Restricted at zero delivery pressure

dictated by the feed section. A screw is restricted if the delivery end restricts the feed end so that polymer is introduced at less than the feed section natural rate. Restriction by the melting section can occur but will be ignored here.

The explanation which follows of what goes on in different screw configurations as indicated by the simple flow theory is limited unfortunately by ignorance of what happens before the material gels. There is a point in a screw where the material has gelled sufficiently to behave as a viscous liquid, when its behaviour can be explained within limits by Equations 5, 6 or 7, and Fig. 15.7. Before this gel point the more or less solid material is conveyed by friction and in restricted screws it is a matter of common observation that the solid becomes compacted. Compacting is in effect a rise in pressure, but it will be neglected for the moment. Also for simplicity the gel point will be assumed stationary and constant viscosity will be taken.

Imagine a screw of constant pitch and depth extruding polythene with zero delivery pressure. After the polythene has melted it occupies less volume than the granules, and consequently at the delivery end the screw channel must be partly empty. Q/Wbh is less than $\frac{1}{2}$ for the whole channel, and Q is the unrestricted delivery rate of the feed section, *i.e.*

$$Q = \eta nS \frac{D_G}{D_S} \quad (9)$$

Here

- η = feed section volumetric efficiency.
- n = revolutions per unit time.
- S = swept volume per turn of the screw.
- D_G = bulk density of the granules.
- D_S = bulk density of the solid.

Suppose a die is put on the barrel, creating a pressure demand. The channel of the screw will now fill back from the delivery end to a point where the pressure demand is satisfied, as shown in Fig. 15.8a. Pressure rise and channel filling must be simultaneous, because if the channel is not full pressure clearly cannot rise, and if the channel does fill then the melt equation applies, and by Equation 4 the pressure must rise since Q/Wbh is less than $\frac{1}{2}$. With increasing delivery pressure the channel fills further back, Q remains the same, and the screw is unrestricted until the channel fills at the gel point (Fig. 15.8a). For greater delivery pressure the screw will be restricted, that is l_e in Equation 5 will be fixed, Q will decrease and the pressure gradient increase.

Output should be proportional to screw speed for an unrestricted screw, and also for a restricted screw under the assumptions made. If the gel point of a restricted screw moved forward with increase of speed instead of remaining stationary as assumed, the ratio of output to screw speed would decrease, however.

Next, consider a screw, the channel width or depth of which is decreased towards the delivery end, though only slightly, so that even for the

smallest values of b or h at the delivery end, Q/Wbh is less than $\frac{1}{2}$. The pressure gradients of Fig. 15.8a would be curves with decreasing slope towards the delivery end, but with this exception, that if $Q/Wbh < \frac{1}{2}$ in a decreasing depth screw the gradient will increase. Apart from changing the shapes of the pressure gradients, the effects of changing channel delivery pressure and speed should be the same as with a constant pitch and depth screw.

Next, suppose b or h change more than in the above screw, so that at some point Q/Wbh is $\frac{1}{2}$. At zero delivery pressure the channel must fill earlier than this point, because as b or h decreases after filling Q/Wbh must increase, and consequently dP/dz in Equation 4 must decrease. Now if Q/Wbh were $\frac{1}{2}$ at filling dP/dz would be zero and its subsequent decrease would give a sub-atmospheric delivery pressure. This leads to the conclusion that when the channel fills Q/Wbh is less than $\frac{1}{2}$.

With increasing delivery pressure the filling point moves back towards the gel point, and b_1 or h_1 in Equation 6 or 7 increases while Q remains constant. Consequently Q/Wbh is $\frac{1}{2}$ at the same place in the screw until the delivery pressure is such that the channel fills at the gel point. For greater delivery pressure than this the screw becomes restricted, b_1 or h_1 is constant in Equation 6 or 7, Q becomes less than the natural feed rate of the feed section, and the point at which Q/Wbh is $\frac{1}{2}$ moves forward. The pressure gradients for such a decreasing depth screw are shown in Fig. 15.8b. Again, output and screw speed should be proportional.

A further case remains. For large reductions in b or h the delivery end restricts the feed end, i.e. Q is less than the unrestricted feed section rate, even at zero delivery pressure. The progression of events for changing delivery pressure is indicated in Fig. 15.8c, drawn for a screw with decreasing channel depth and a "metering" section of fixed dimensions at the delivery end. As delivery pressure is raised output Q should decrease and the point at which Q/Wbh is $\frac{1}{2}$ moves forward. At some delivery pressure Q/Wbh will equal $\frac{1}{2}$ in the metering section. With even greater delivery pressure Q/Wbh is less than $\frac{1}{2}$ for the whole screw. The term "metering section" evidently can be a misnomer, as it does not meter independently if gelling occurs in the tapering part. If gelling were not to occur until the beginning of the fixed dimension portion, pressure would rise linearly, and the metering section would meter independently.

For decreasing depth screw without a metering section the pressure curves will be broadly similar in shape to Fig. 15.8c, but not linear in the front part. The pressure gradient in a decreasing pitch screw should always decrease towards the delivery end, but otherwise the effects should be similar.

The feed section output may be restricted by the screw at a point before gelling, but no account can be taken of this as the melt theory is the only tool available at the moment.

Some conclusions can be drawn from the qualitative application of the simple melt flow theory to screws fed with solid granules.

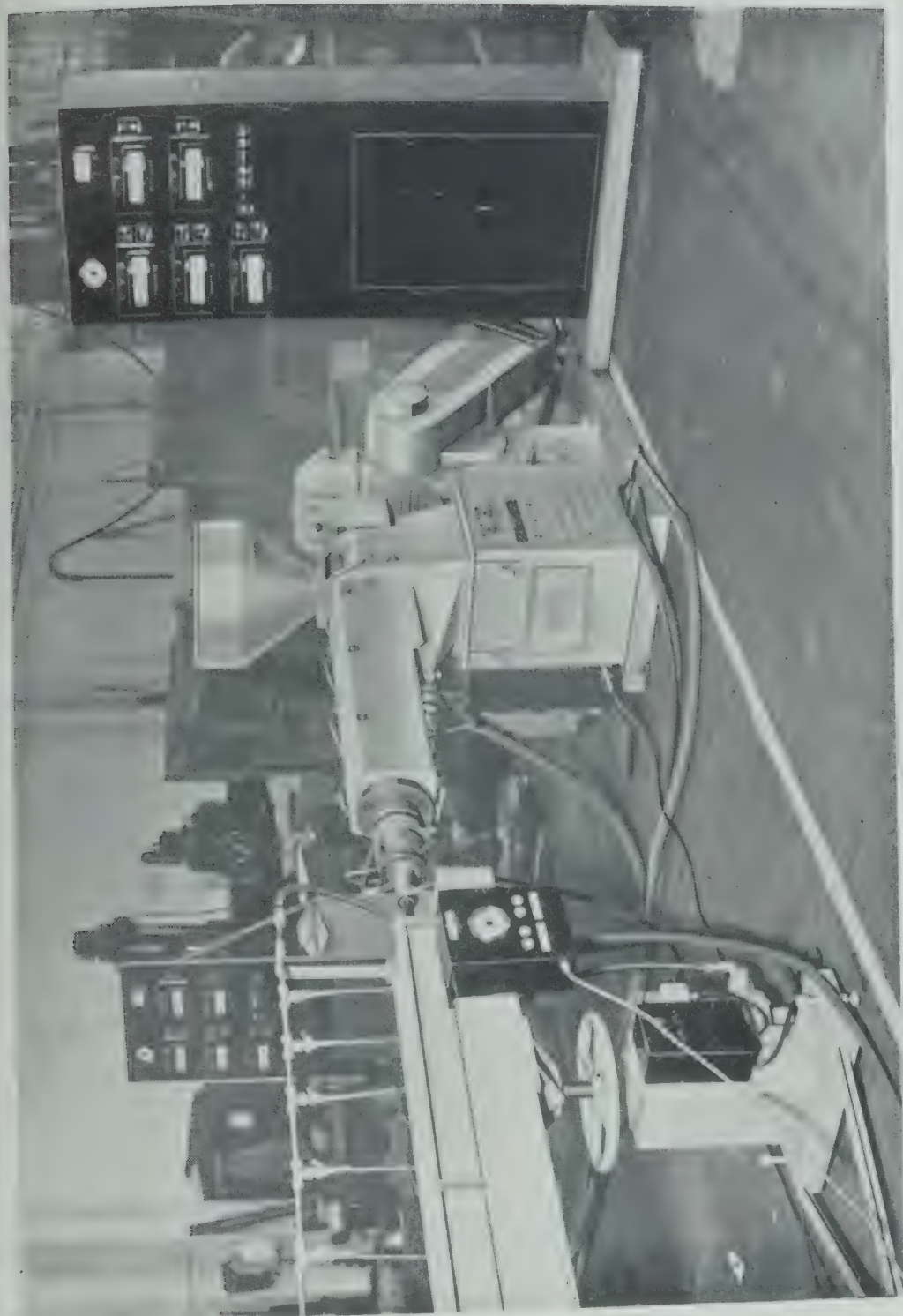


Plate 15. 1. Single screw extruder, 2½ in. (Projectile & Engineering Co. Ltd.)



Plate 15.2. Polythene screw for the $2\frac{1}{2}$ in. extruder shown in Plate 15.1

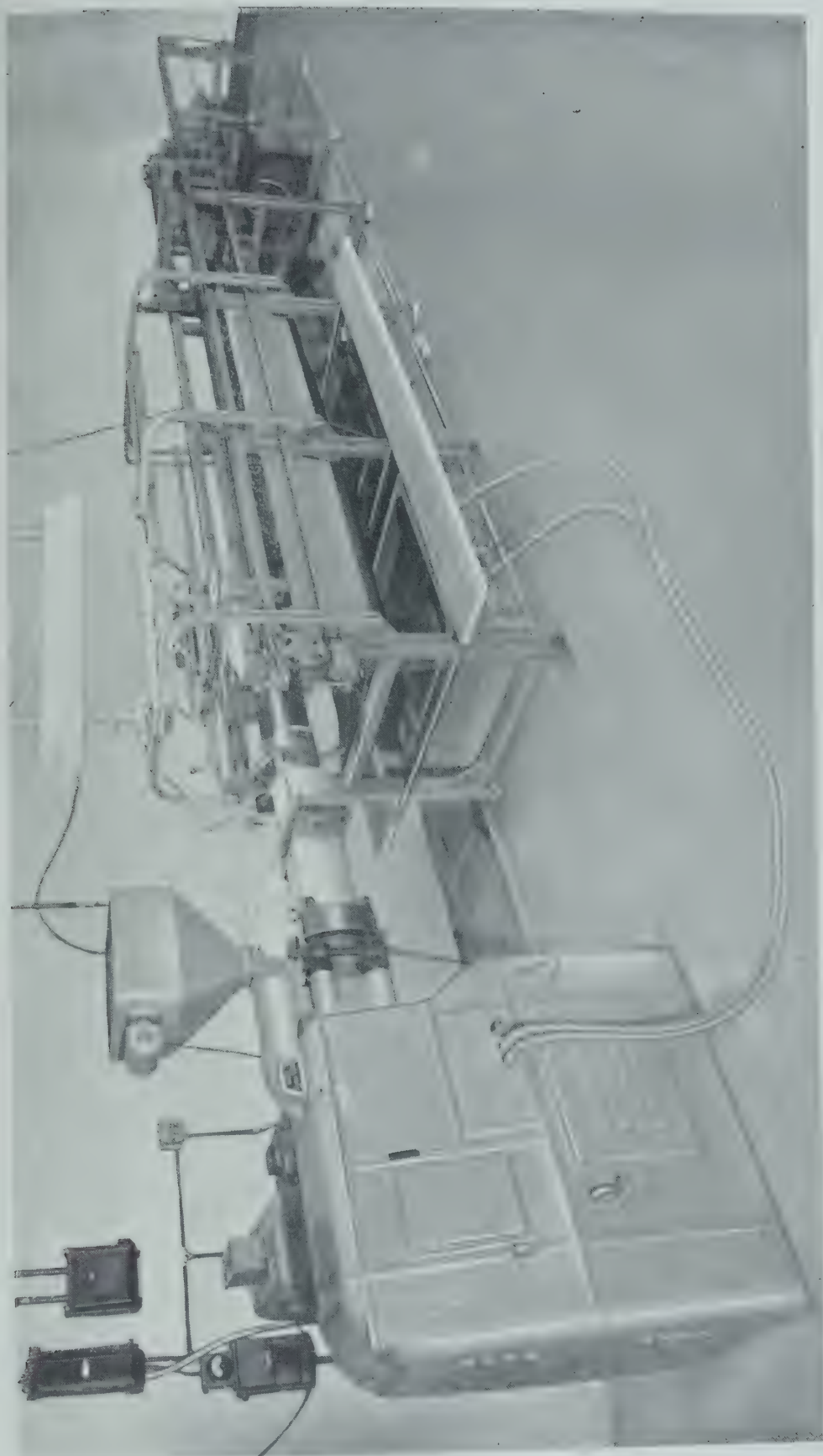


Plate 15.3. Twin screw extruder (R.G.100) and take-off equipment producing $6\frac{1}{2}$ in. o.d. \times $5\frac{3}{4}$ in. i.d. polythene tubing R. H. Windsor, Ltd.)

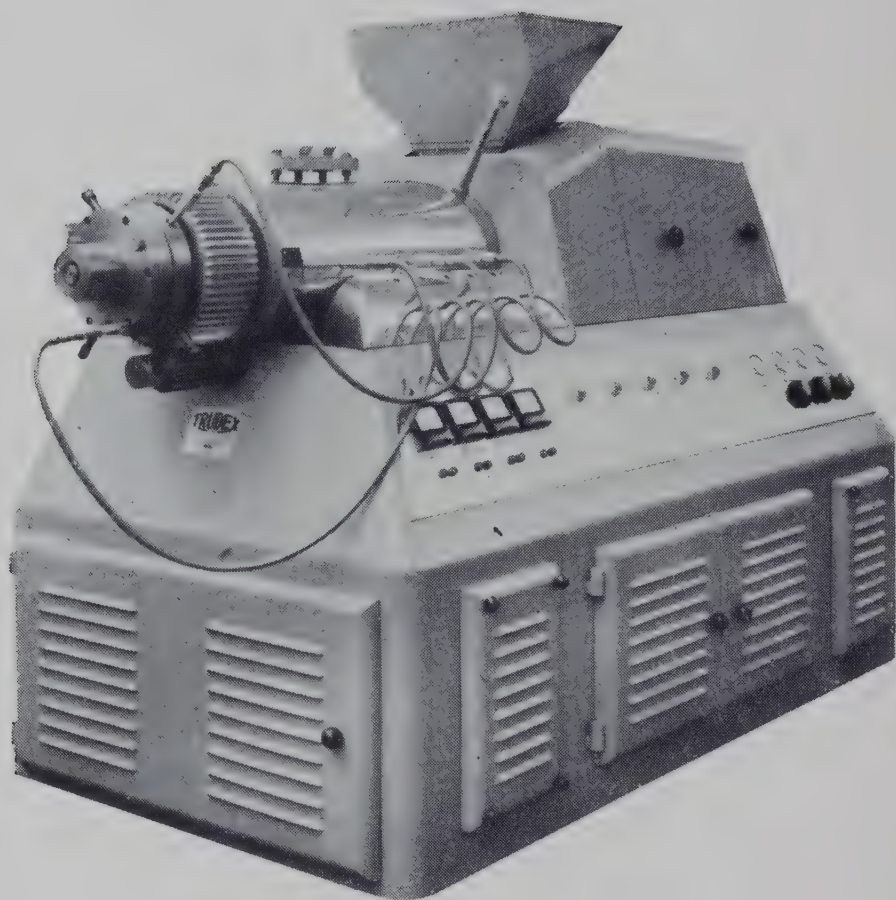


Plate 15.4. Trudex twin-screw extruder

First, screws which are unrestricted at zero delivery pressure will continue to give the same output with increasing delivery pressure until the channel fills at the gel point. For greater delivery pressures than this such a screw is restricted and output begins to drop.

Secondly the output of screws which are restricted decreases continuously with increasing delivery pressure. If channel depth h is reduced rather than breadth b to cause the restriction, the rate of decrease in output is lower and such a screw would have a very high delivery pressure potential.

Thirdly, output should be proportional to screw speed under the assumptions made.

Finally, greater mechanical working would be expected with a restricted screw than an unrestricted screw. Whether a screw will be restricted or not is clearly important. It depends on pressure, channel dimensions, melt viscosity, and the position of the gel point. The big stumbling block is the last. However, it is easy to find how a screw is operating in a particular case by measuring output without the die.

This attempt to explain what happens in different screw configurations is based on the simple melt flow theory, and consequently is bounded in its application by the assumptions made. Most serious shortcomings are:

- (a) Compression of the solid in a restricted screw is equivalent to a rise in pressure and this has been ignored.
- (b) The gel point has been assumed stationary. In fact it will move with change in output and screw speed.
- (c) The effects of viscosity gradients can be great. Viscosity will decrease along the channel as the polythene heats up, which will steepen the pressure gradient early on and flatten it later. Further, it is most likely that viscosity gradients exist across the stream. Heat is usually being added or removed at the barrel wall which will cause temperature and consequent viscosity gradients, though this should be lessened by the rotational component of the velocity mentioned earlier, which helps to homogenize the mass by carrying heat to or from the interior. Internal shearing may also produce temperature gradients. As polythene is not a Newtonian fluid its so-called "viscosity" changes with rate of shear as well as with temperature, and rate of shear is likely to vary across the channel. Very frequently heat is removed by screw cooling which increases the viscosity close to the screw and usually reduces the output considerably. The effect can be visualized as a reduction in the depth of the screw channel. It is used to promote mixing and mechanical working. Finally a thin layer of polythene on the barrel may be sheared vigorously and heated as the screw flights pass over. At high delivery pressure this layer can get so hot that all the material goes round with the screw and extrusion stops.
- (d) It was assumed that the simple melt flow equation applies. This is an approximation which applies well only for high b/h ratios.

POLYTHENE

All these features distort the simple picture given earlier. One is led to the conclusion that the reality of an extruder screw is exceedingly complex, but it is thought that the explanation given is qualitatively correct. Pressure and temperature measurements in polythene extruders have been reported in the literature^{3, 5}.

SCREW DESIGN

The choice lies broadly between a restricted and an unrestricted screw. Experience shows that a restricted screw is better for polythene because the polymer is worked more intensively. A homogeneous melt is produced giving good surface finish on the product. Unrestricted screws have their uses for plastics which degrade with excessive mechanical working.

Currently a polythene screw is usually designed with a fairly deep channel at the feed pocket to give a feed rate in excess of what the delivery end will pass. A feed section volumetric efficiency of 30% is a reasonable figure for calculating the unrestricted feed rate with Equation 9. The bulk densities for various cuts of polythene are given in Table 15.1.

Reduction in flow area of about three to one between feed and delivery ends is usual. This should restrict the screw for delivery pressures met in practice. The restriction is better carried out by reducing the channel depth, keeping a constant pitch. It is common to make a third to a quarter of the screw at the front with constant depth. This should improve the pressure potential of a screw slightly compared with one tapering uniformly right to the delivery end though otherwise similar. However this difference is marginal. A screw length 15 times the diameter should be satisfactory.

Faced with the problem of predicting the output of a restricted screw, the complexity of operation has naturally encouraged designers to try the simplest possible solution to see how it works. For a screw with a metering section, gelling is assumed to occur at the beginning of the constant depth section and an average viscosity is used.⁴ In general results agree tolerably with practice where screw cooling is slight. It is well worth using this method in the absence of anything better, though it should be looked on only as a guide to performance.

Table 15.1. BULK DENSITIES OF DIFFERENT CUTS OF LOW DENSITY POLYTHENE
LB. PER CUBIC FOOT

Masson cut irregular chips	Spaghetti cut $\frac{3}{8}$ in. cylinders	Cube cut $\frac{1}{2}$ in. cubes	Caviare cut $\frac{1}{2}$ in. spheres
18.9	31.6	27.5	33.7

D_G for a low density polythene 57.5 lb/cu.ft.; high density polythene 59.5 lb/cu.ft.

If it is desired to use a uniform taper for the whole screw length, a similar guide may be obtained if gelling is assumed to occur about half way along the screw. Equations 6 or 7, whichever applies, will give the flow for a particular delivery pressure. An example is given in the next section.

Should an unrestricted screw be required for any purpose, output prediction is easier as one needs to know only feed section volumetric efficiency and the bulk density of the granules. Whether screw operation is unrestricted can be checked roughly assuming that gelling occurs halfway down the screw and using a constant viscosity. Screw design may be influenced by the need which is sometimes met for compounding pigments with the polythene.

For good compounding it is usually necessary to increase the back pressure on the screw by a smearhead or other restriction and to accept

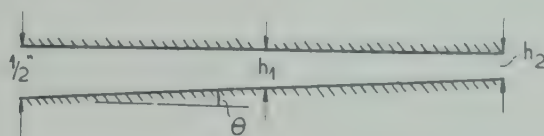


Fig. 15.9. Diagrammatic representation of tapering channel

the consequent decrease in output. The greater back pressure engenders greater shear throughout the material as a whole, as may be seen from Fig. 15.6, and mixing is promoted. Long screws are also an advantage for mixing because more shearing is done. The high shear rates with consequent high heat release mean that a good deal of cooling is necessary. It is sometimes necessary to add a special mixing head to the front of a screw for mixing difficult pigments.

Opinions differ on the relative merits of single or multiple start threads for extruder screws. The heat transfer rate to the material and internal mixing should be greater with a multiple start screw owing to the greater frequency of scraping the barrel wall. Against this, if a multiple start screw works against a high delivery pressure one of the channels may stop extruding, sometimes with the result that molten polymer is forced back into the feed hopper and blocks it. Usually either type of screw works well with polythene and the choice is not particularly important.

EXAMPLE OF SCREW DESIGN

This example illustrates the design of a screw which is unrestricted at low delivery pressure but becomes restricted at moderately high delivery pressure, so that if homogenization is not good enough at high output when unrestricted, artificial increase of pressure with a smearhead will restrict the screw and improve homogenization.

The specification is as follows: 3 in. diameter screw; constant pitch of 3 in. single start; varying depth; flight width $\frac{1}{4}$ in.; length 45 in.; unrestricted output 230 lb/hr. at 60 rev/min. Screw to become restricted

at a delivery pressure of 1500 lb/sq.in. Material—"Caviare" cut density polythene, melt flow index 2.

Feed section

230 lb/hr. at 57.5 lb/cu.ft. is 1.9 cu.in./sec. of solid.

In Equation 9

$$\begin{aligned} Q &= 1.9 \text{ cu.in./sec.} & D_G &= 33.7 \text{ lb/cu.ft.} \\ \eta &= 0.3 & D_S &= 57.5 \text{ lb/cu.ft.} \\ n &= 1 \text{ rev/sec.} \end{aligned}$$

from which $S = 10.8$ cu. in. per sec.

This swept volume is given by a channel depth of $\frac{1}{2}$ in.

Melt section

Mean helical path length along the screw is 126 in. If gelling occurs half-way down it, the length of the melt section is 63 in.

$$\left(1 - \frac{h_2}{h_1}\right) - \frac{Q}{Wbh_2} \left(1 - \frac{h_2^2}{h_1^2}\right) = \frac{gh_2P_e}{6\mu W} \cdot \tan \theta \quad (1)$$

Referring to Fig. 15.9

$$h_1 = \frac{0.5 + h_2}{2} \text{ and } \tan \theta = \frac{0.5 - h_2}{128}$$

at 1500 lb/sq.in. and 60 rev/min.

$$\begin{aligned} Q &= 1.9 \text{ cu. in./sec.} & b &= 2.75 \text{ in.} \\ W &= 7.33 \text{ in./sec.} & P_e &= 1,500 \text{ lb/sq.in.} \end{aligned}$$

If the extrusion temperature is 190°C the viscosity of polythene melt flow index 2, at 150°C is a suitable figure to use.

$$\frac{\mu_a}{g} = 0.28 \text{ lb.sec/sq.in.}$$

Using these values the solution of Equation 7 by trial and error is $h_2 = 0.155$ in. and $h_1 = 0.328$ in.

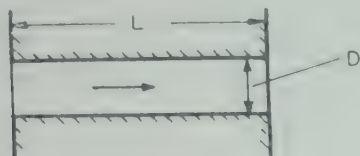
By substituting these values in Equation 7 the output can be found at delivery pressures greater than 1,500 lb/sq. in. At 4,000 lb/sq.in. the output is 1.57 cu.in./sec and $Q/Wbh_2 = \frac{1}{2}$. Below 4,000 lb/sq.in. then, the maximum pressure occurs in the screw upstream from the delivery end. If the maximum working pressure in the barrel is 5,000 lb/sq. in., a reasonable figure for a barrel of this size, then with this screw the barrel is safe providing the delivery pressure is not allowed above 5,000 lb/sq.in.

FLOW OF POLYTHENE IN DIES

Calculation of die pressure is useful for predicting how a screw will perform and for mechanical stressing.

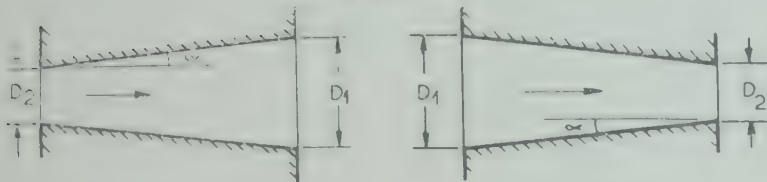
Most dies can be broken down into a series of simple shapes, and the pressure drops across them can be added to give the total pressure at the

TUBE



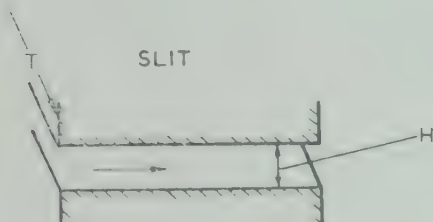
$$\Delta P = \frac{128 \mu_a Q L}{\pi g D^4} \cdot \text{Shear Rate} = \frac{32 Q}{\pi D^3}$$

CONICAL SECTIONS



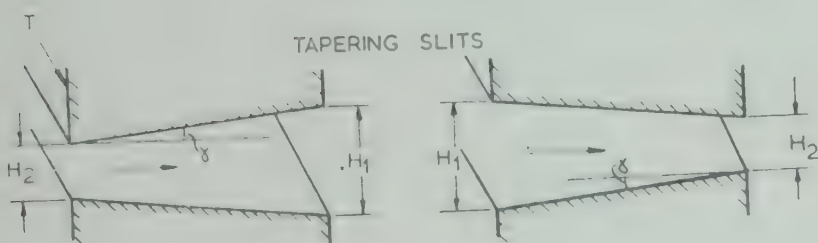
$$\Delta P = \frac{64}{3 \pi} \frac{\mu_a Q}{g \tan \alpha} \left[\frac{1}{D_2^3} - \frac{1}{D_1^3} \right] \cdot \text{For small } \alpha$$

SLIT

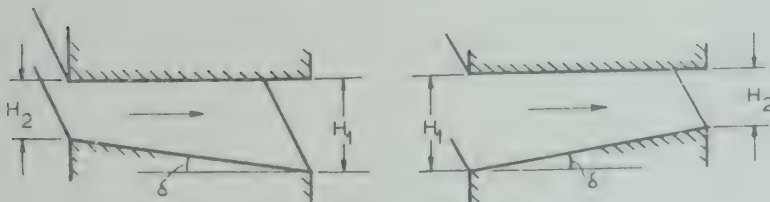


$$\Delta P = \frac{12 \mu_a Q L}{g T H^3} \cdot \text{Shear Rate} = \frac{6 Q}{T H^2}$$

TAPERING SLITS



$$\Delta P = \frac{3 \mu_a Q}{g T \tan \gamma} \left[\frac{1}{H_2^2} - \frac{1}{H_1^2} \right] \cdot \text{For small } \gamma$$



$$\Delta P = \frac{6 \mu_a Q}{g T \tan \delta} \left[\frac{1}{H_2^2} - \frac{1}{H_1^2} \right] \cdot \text{For small } \delta$$

Fig. 15.10. Pressure drop of a "Newtonian" fluid in various channels

die entry. Fig. 15.10 gives expressions for the pressure drop of a Newtonian fluid in streamline flow through various simple shapes. Pressure drop varies linearly with output and viscosity. The expressions for tapered sections apply strictly only to small tapers.

It is quite simple to use Equation 8 and obtain equivalent expressions which take into account the change of viscosity with rate of shear which occurs with polythene. However, the slightly simpler alternative is preferred of using an apparent viscosity μ_a , corrected for shear rate, in the Newtonian formulae. The effect of this non-Newtonian behaviour is that as output and therefore shear rate increases, the apparent viscosity decreases and the pressure does not increase in proportion.

Apparent viscosity at a shear rate of 25 sec^{-1} is given in Fig. 15.11. Rate of shear can be calculated for the channel under consideration from the expressions given in Fig. 15.10. If the channel is tapered, the shear rate at the mean cross section will do. The ratio of viscosity at the shear rate to that at 25 sec^{-1} is given in Fig. 15.12 and the viscosity ratio multiplied by the value obtained from Fig. 15.11 gives the apparent viscosity for use in the appropriate pressure drop equation. The curve of Fig. 15.12 is a mean of many established from data obtained by Clegg⁶ for low density polythene of melt flow indexes 0.2, 0.7, 2, 7, 20 between 150°C and 250°C .

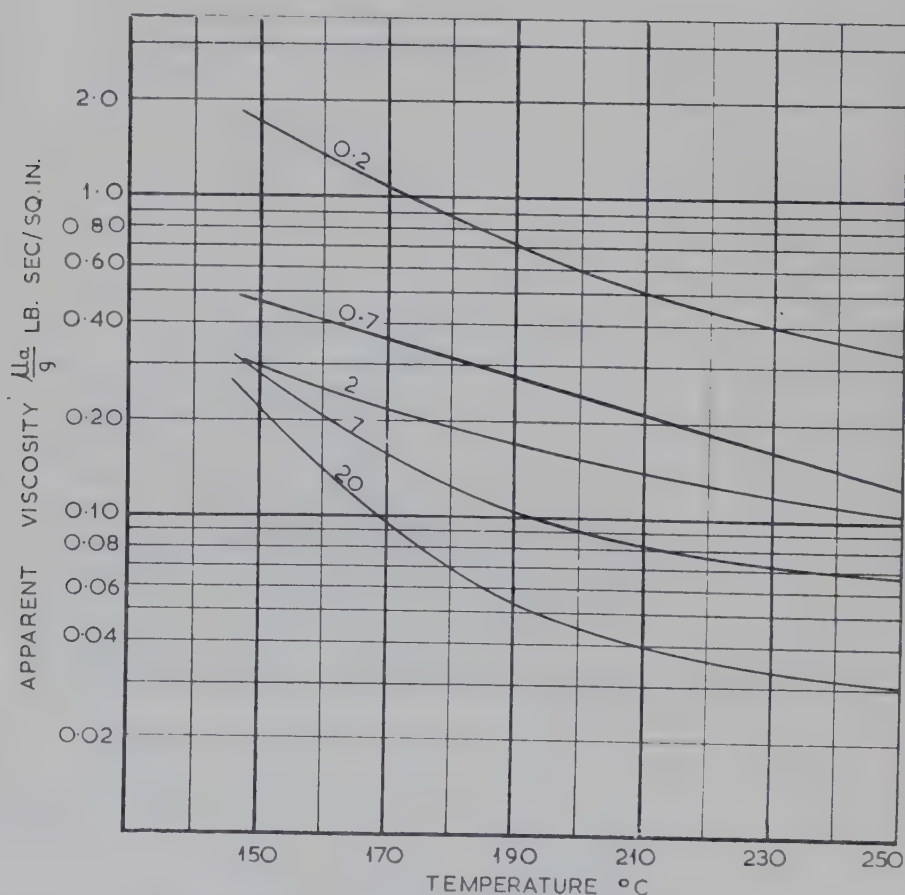


Fig. 15.11. Apparent viscosity of low density polythenes. Shear rate 25 sec^{-1}

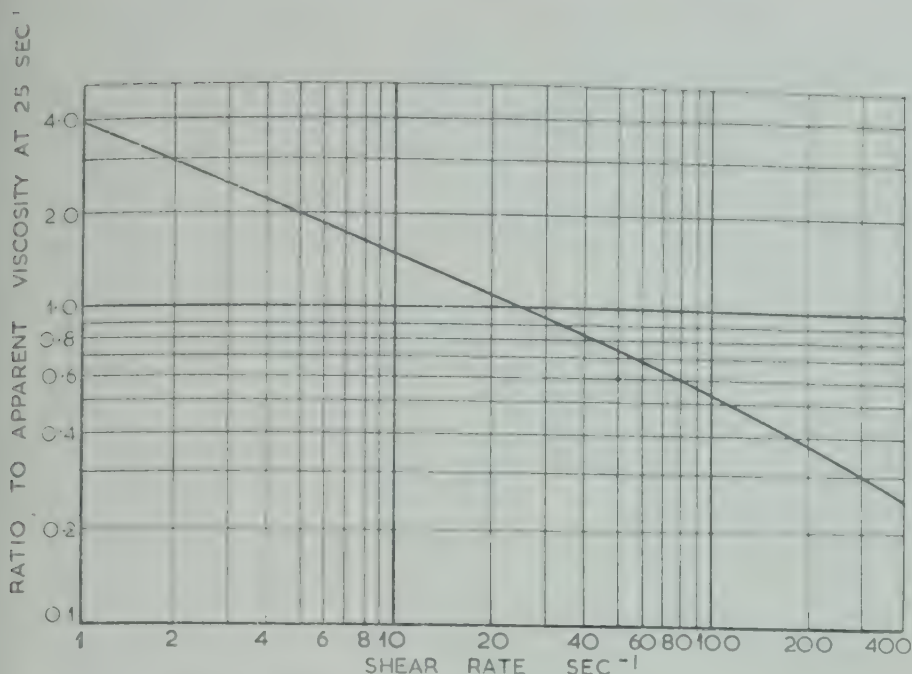


Fig. 15.12. Correction curve for shear rate (Note.—This curve is a mean of many different curves for melt indexes from 0.2 to 20 and temperatures 150°C to 250°C. It gives results to a first order approximation only)

The method outlined applies to a polythene melt being extruded from a die at the same temperature as the melt. Differences in these temperatures can affect pressure drop by changing the viscosity of the layer next to the wall.

It is worth noting that both the pressure rise in the screw and the pressure drop across the die depend linearly on apparent viscosity. Thus a screw and die combination working a particular grade of polythene should behave similarly and give the same output with a different grade, but the pressure at a particular point will change in proportion to the apparent viscosity.

POWER CONSUMPTION

No data appear to be available for calculating the length of screw channel needed to melt the solid polymer, either by power supplied by the screw or heat conduction from the barrel.

A method has been given² for calculating power consumption in the molten section of a single screw extruder if the viscosity of the material is constant, assuming the length of the section is known. Power is used both in the channel and on the tops of the screw flights. The distance between the tops of the flights and the barrel is small so the rate of shear on the amount of material is high and a large proportion of the work is dissipated in this region. This means that the material is likely to heat up more in this region with consequent drop in viscosity; the extent of this heating is unknown, and consequently a power consumption calculation for the molten section based on the same viscosity for channel

and flight top is likely to give a high result. For these reasons it is difficult to predict the length of screw channel needed to obtain a certain work input to the material. In practice about 15 h.p. for every 100 lb polythene extruded per hour covers the demand for most purposes.

THE EFFECT OF EXTERNAL CONTROLS ON EXTRUDER PERFORMANCE

The most important external controls on an extruder are screw speed, barrel heating or cooling, hopper cooling, and screw cooling.

When there is no delivery pressure, or when delivery pressure is constant, output should be proportional to screw speed. When working with a particular die the relation will be somewhat more complicated as the pressure depends on the pressure-flow properties of the polythene through the die in use, the position of the gel point etc., but in general output will increase with screw speed. However, as screw speed is increased there usually comes a point at which the material emerges partly unmelted unless special precautions are taken. The problem is basically one of control. For economic reasons it is undesirable to use too large a motor, and at the same time there is a practical limit to the amount of power which can be supplied by heaters. A ratio of applied heat to mechanical work input must be reached and maintained so that the driving motor required is not too large and the amount of power needed by the heaters is reasonable. Also the screw and barrel must be sufficiently long to absorb the work and heat provided. Increasing interest is being shown by manufacturers in the possibilities of higher speeds with corresponding higher outputs from small machines, and the associated difficulties may well be overcome, without too much sacrifice of operational flexibility.

Heating of extruder barrels is done either electrically using conduction or induction, or with fluids.

It is often found that an extruder will not deliver material unless cooling water is circulated close to the hopper. The reason is probably that heat conducted back along the barrel towards the hopper melts a thin layer of polymer on the barrel surface. This layer acts as a lubricant so that the feed does not grip the barrel wall and get carried forward. The effect of cooling water is to prevent formation of a lubricating layer.

A further and most drastic control available on single-screw extruders is screw cooling. It generally tends to reduce output and increase the mechanical working of the polymer. Screw cooling is often necessary as otherwise the material may be extruded too rapidly and not uniformly melted. Though screw cooling will always be a useful control on an extruder its use may become less necessary as screw designs are improved.

Surging is sometimes a problem in extruder operation. The chain of events leading to surging has not really been explained, but with polythene the result is usually a cyclic variation in power demand which causes a

change in screw speed and therefore output. The change in output depends mainly on the torque-speed characteristics of the driving motor. Adjustment of operating conditions can often help and screw design can certainly affect surging. Sometimes it may be necessary to govern the motor. Even so surging may occur with a constant screw speed if there is an intermittent hold-up of material in the hopper. Unfortunately, there is no universal panacea for preventing surging, and each case must be dealt with separately.

The temperatures and conditions required for extruding various products are indicated in other chapters. In general the harder the material the higher the temperature required. The limited experience available on extrusion of high density polythene shows that they can usually be processed at the same temperatures as low density polythene of the same grade number.

The regulation of external controls depends on the type of extruder and the product, and good operating conditions must be found by trial.

CONCLUSIONS

The operation of both single and twin screw extruders is complex, and consequently quantitative design is difficult. The gaps in knowledge are mainly concerned with conveying and melting of polymer granules.

Designs are mainly the result of guesswork and tradition, but fortunately polythene is a docile material to extrude compared with most plastics, and there are few extruders on the market at present which cannot be made to work with the softer grades of polythene at least. However, this state of affairs is fundamentally wrong. The extruder should be tailored to the plastic, not the converse.

Developments in the next few years should be interesting. Screw cooling in single-screw machines is clearly undesirable as it reduces output, and as more is learnt this cooling may be eliminated perhaps by using longer screws. Higher screw speeds may well pay dividends. The feed section output capacity of both single and multiple screw machines is usually far in excess of what the screw actually deliver, and it is to be hoped that more advantage will be taken of the very high potential outputs of screw extruders.

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THE EXTRUSION OF POLYTHENE: CABLE COVERING

R. M. FAIRFIELD

WHEN polythene became commercially available just before the second world war, it was immediately appreciated from a study of electrical and physical characteristics that the material was of great interest to the cable industry. Its first use was for submarine cable and later it had extensive applications in the radio frequency field. In view of the rapid development of radar systems, demanding much higher transmission frequencies, the production of polythene radio frequency cables increased considerably and this, in turn, necessitated the development of improved processing techniques and equipment.

Briefly, the machinery required for the extrusion of polythene on to conductors can be divided into two main sections. Firstly the extruder, usually fitted with a cross-head, for the application of the polythene to the conductor, and secondly, suitable ancillary plant for winding the conductor through the extruder head at constant speed, cooling the molten polythene covering, and winding the product on to a drum. Because of the difficulty of maintaining a constant speed through the head, it is not sufficient merely to take the conductor from one drum, pass it through the extruder head and then wind it directly on to the

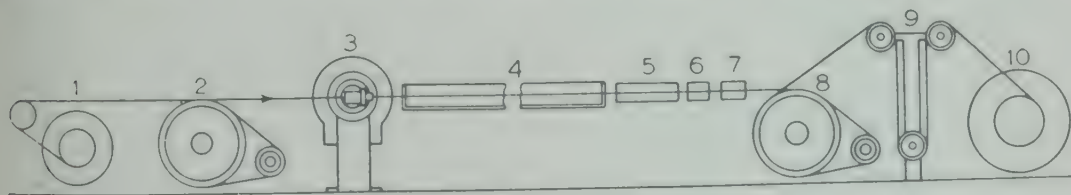


Fig. 16.1. General layout of a cable extrusion plant

- | | |
|-------------------------|------------------------|
| 1. Input drum. | 6. Diameter gauge. |
| 2. Input capstan wheel. | 7. Eccentricity gauge. |
| 3. Extruder. | 8. Capstan wheel. |
| 4. Cooling trough. | 9. Tension controller. |
| 5. Spark tester. | 10. Output drum. |

take-up drum. The usual practice is to pull the conductor through the head by means of a capstan wheel driven at constant speed, after which it is wound on to the output drum, the speed of which is regulated to compensate for the build up of cable. The general lay-out of these essential items is shown in Fig. 16.1 together with added refinements for

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the control of the process. A fuller description of each of the components is given in the sections to follow.

EXTRUDERS*

Early attempts to extrude polythene melt index 20 were made on modified rubber extruders which had short scrolls and steam heated barrels and heads. The chief modifications consisted of fitting electrically heated extension necks and die boxes. When fed with polythene, pre-heated in a steam heated open mill, these machines produced cable with a moderate degree of success. The provision of longer barrels and scrolls improved matters considerably, and together with addition of roller feeds enabled more constant output from the machines to be obtained.

On the introduction of the harder melt index 7 polythene, the feeding method was still widely practised because steam heating and the characteristics of the scrolls used at that time limited the transfer of heat to the polythene during its passage through the barrel, making continuous feeding impracticable. Even when feeding hot material the desired extrusion temperature could not easily be obtained in the barrel alone and large heated heads and extension necks were used to raise the temperature of the polythene further. A serious drawback to this method was the necessity for a mill to be working all the time the extruder was running, and the advent of the even harder grades of polythene requiring still higher extrusion temperatures made the provision of more suitable extruders imperative.

The usual modern practice is to feed the polythene into the machine as cold granules thus dispensing with the pre-heating mill, and modern extruders have been specifically designed for this purpose. The granules are introduced into the barrel by a simple hopper, thus avoiding the necessity for refinements such as roller feed or vibrators. It is desirable to *condition* the polythene for extrusion completely in the barrel, using the head merely as an applicator, and for this purpose electrically heated barrels and long scrolls are used. The length of the barrel is usually expressed as a multiple of the scroll diameter, and most modern machines have barrels with length/diameter ratios of 12 : 1 or 15 : 1, and occasionally as much as 20 : 1. The barrel is heated by a number of electric elements so that the temperature can be varied along its length. Usually the barrel is divided into two or three zones, in each of which the temperature is thermostatically controlled. The design of the heater elements is important as failure of these is probably the most common source of trouble on extrusion machines. The power required for heating the barrel obviously varies according to its size, but it is better to be generous rather than to underrate the heaters, as this gives better reliability and permits rapid heating from cold. As an example, a very convenient arrangement for a 2 in. extruder having a barrel with a length of 15 : 1 diameter ratio is to use six heaters each of 800 watts. These heaters are arranged in three

* See Chapters 17 and 18.

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groups of two, each pair being separately controlled. With this arrangement the working temperatures for polythene, which are in the region of 200°C , can be reached from cold in about 15 mins.

When feeding granules of polythene a considerable proportion of air is also introduced, and to help in the removal of this the scrolls are designed to compact the polythene during passage towards the delivery end of the barrel. This can be achieved either by shortening the pitch of the scroll progressively from the input end, keeping the root diameter constant, or by increasing the root diameter and maintaining constant pitch. The latter is the better method as it allows a greater area of polythene to be in contact with the barrel per convolution of the scroll and thus assists heat transfer. The ratio of the volume contained in the first convolution of the scroll to that in the last convolution is known as the compacting (or compression) ratio, and for polythene, scrolls with compacting ratios of 2 or 3 to 1 are satisfactory.

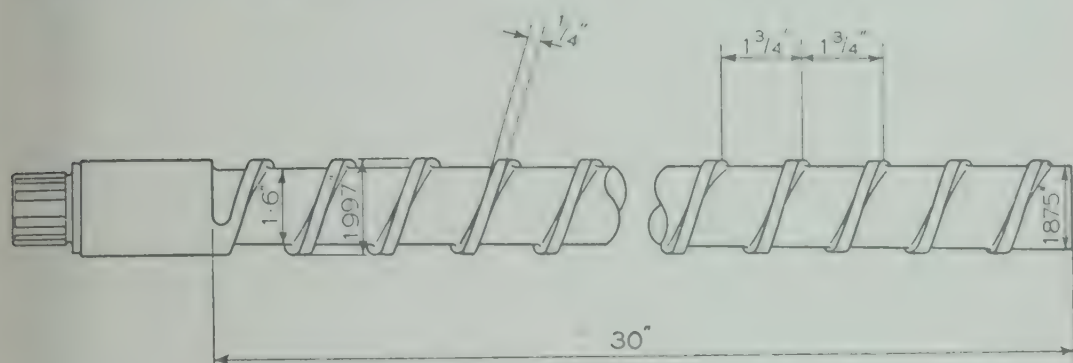


Fig. 16.2. Typical scroll for 2 in. extrusion machine having a length diameter ratio of 15 : 1 and a compacting ratio of 3 : 1

Scrolls are available having single or double starts and occasionally three or four starts. The advocates of multiple start scrolls maintain that they give a more regular feed into the head, but in general there is very little difference in performance when using either single or double start scrolls. Irregular feed into the head would result in diameter variations of the finished cable, but these can also be caused by changes in the rotational speed of the scroll and in the speed of the conductor through the head. The design of a typical scroll is shown in Fig. 16.2.

The material from which the scrolls are made should be selected with care. Many scrolls are made of a hard alloy steel and chromium plated, but experience has shown that unless special attention is given to the quality of the chromium plating, cracking and flaking will occur. A suitable material for the scroll is nitriding steel to British Standard 970, En 40 B or C, which after heat treatment has a Brinell hardness of 850-900.

It is desirable that the scroll speed should be capable of adjustment over as wide a range as possible, preferably from zero to about 60 or 80 rev/min. The adjustment can be achieved in a number of ways, the most common being to drive the extruder by a variable speed a.c. motor, which usually gives a speed range of about 3 to 1. The drawback to this

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method is that the characteristics of the usual type of a.c. motor provide very little power at the lowest speeds. Better, though more expensive methods are to use a fixed speed a.c. motor in conjunction with either a variable hydraulic gear or an electro-magnetic coupling both of which give a continuous range of speeds from zero to the top limit. Probably the best method of all, from technical considerations, is to use a variable speed d.c. motor fed by a Ward Leonard set or a mercury arc rectifier, the latter being slightly cheaper. When using a mercury arc rectifier the speed at any given setting is very constant. Adjustment of speed over a range of about 8 to 1 is made by grid control of the voltage output of the rectifier in the low speed range, and by field control at higher speeds.

It has been found that wire mesh screens, supported on a backing plate drilled with $\frac{1}{8}$ in. diameter holes fitted in the end of the barrel, are an aid to good extrusion, as otherwise irregular flow may result in variation of cable diameter. The actual selection of a screen pack depends very much upon the operating conditions, but a typical pack would consist of one 30 mesh supporting a 60 and a 100 mesh screen.

EXTRUDER HEADS

The extruder heads used for cable covering are almost invariably scroll-heads, though machines do exist in which the wire passes through the scroll to a straight-through head. Since polythene is extruded in the fluid state and, when containing suitable antioxidant, is relatively heat stable, there is little danger of scorching or charring, and hence the design of the extruder head can be comparatively simple. There is therefore, less necessity for the careful streamlining of the head which is essential with some other materials. Polythene was first extruded on machines with large old fashioned heads slightly modified to permit additional heating. Later, when electrically heated barrels and suitable scrolls were developed, the polythene emerged from the barrel at the correct temperature for extrusion so that additional heating in the head was not required, and therefore the size of the head could be reduced considerably, sufficient heating being applied merely to prevent loss of temperature. The die is often fitted with a separate heater and is maintained at a slightly higher temperature than the mass of the polythene flowing through the head, in order to give a good polish to the cable. There are many types of extruder heads, and both manufacturers and cable makers have designs with special features many of which are covered by patents.

The head in Plate 16.1 is diagrammatic but indicates all the necessary points. The polythene entering the head is turned through a right angle and emerges from the "female die" situated at the side of the head. Passing through the head is the "core tube", on the end of which is the "core die" or "male die", the orifice of which is very slightly larger than the conductor to be covered. The tube is capable of adjustment both along the axis of the head and at right angles to the axis so that the male die can be adjusted to be coaxial with the female die and a convenient distance away from it.

the distance depending largely on the size of the cable to be extruded. The conductor passes through the core tube and the covering is applied in the small annular space between the dies, the forward movement of the conductor in the close fitting male die preventing polythene flowing back into the core tube.

Many variations on this basic design are possible, one being that the lateral adjustment of the dies is obtained by movement of the female die while the core tube is held rigid in the head by means of a spider. A head of the type described needs some skill on the part of the machine operative for its correct adjustment, which may take an appreciable time. To overcome this, some heads are made in which no adjustments at all are required, the correct die sizes and relative spacing being determined previously. The head and dies are manufactured to very close limits and the design is arranged so that the dies are rigidly and accurately located. As the engineering of this type of head must be of the finest order, and also as a matched pair of dies is required for each size of cable, these heads are only economical where a large quantity of any given size of cable is to be made. A head of this type is shown in Plate 16.2. It should be noted that the core tube of this head is streamlined to prevent material lodging in the head for any considerable time. This feature, while not of great importance for polythene, is very helpful for preventing scorching and charring of other extrudable materials.

The fixed heads of the type illustrated in Plate 16.2 are expensive to make largely because of the intricate shape of the core tube, and a simpler type of self-centring head shown in Plate 16.3 developed mainly for nylon extrusion, has been found quite satisfactory for polythene. It should be noted, however, that this type of head is unsuitable for p.v.c. extrusion, and this is of importance when selecting a head for a general purpose machine to be used for the extrusion of both polythene and p.v.c.

DIE DESIGN

It is very difficult to specify the dimensions of dies for satisfactory extrusion of particular cables. Generally the design is not really critical but individual cable makers adopt that which is most suitable to their particular operating conditions. In general, the male die should be as close a fit on the conductor or cable passing through it as possible, the actual clearance varying with the size and type being covered. For example, when insulating a single wire of 0.044 in diameter, the clearance need only be about 0.002 in. but, when sheathing a multicore cable whose diameter is about 0.25 in., a clearance of 0.008 in. would not be excessive. When using fixed centre heads it is important that the clearance be kept as small as possible as otherwise eccentricity of the conductor will occur.

The type of female die used depends largely on whether the polythene is being applied to a conductor or to a previously insulated core. When used for sheathing core, the diameter of the die is generally chosen to be slightly less than the desired final diameter of the extruded cable. The selection of the length of the parallel portion (or land) and the distance

between this die and the male die are points at which most variations appear between different cablemakers. When using adjustable centre heads the use of long lands and widely separated dies is likely to give rise to difficulties during adjustment due to polythene flowing back into the core tube. Also, it is often desired merely to apply a tube of polythene over an irregularly shaped core, either to produce an air-spaced cable or to minimise adhesion between core and sheath. In these cases the land on the female die must be short or even non-existent, and the dies positioned near together. If it is intended to fill all the interspaces between cores, a longer land must be used, and usually a larger distance between the dies. A typical arrangement is shown in Fig. 16.3.

Many cablemakers use similar dies for insulating conductors but another type of female die is rapidly growing in favour, particularly for the application of very thin walls of polythene of 0.004 in. to 0.010 in. on fine wires. This die has a long tapered land, the smaller diameter of which is slightly larger than the desired final size of the cable. The end of the male die is situated near the beginning of the tapered land. The principle of operation of this die is that the acceleration of the polythene along

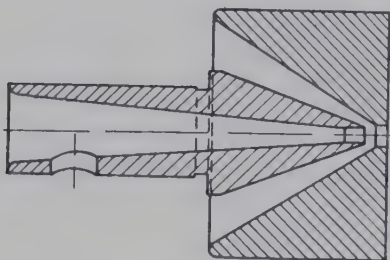


Fig. 16.3. Conventional male and female die arrangement

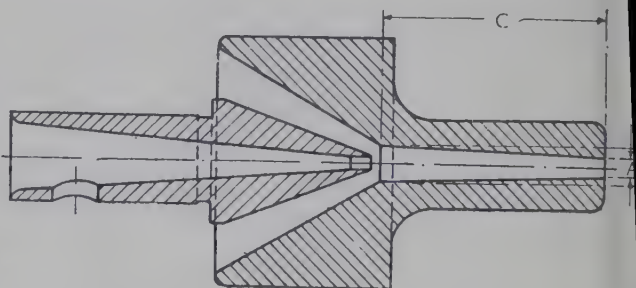


Fig. 16.4. Core and die arrangement for the application of thin walls

the decreasing cross section of the die helps to keep the fine conductor in the centre. Requirements for this type of die are:—

- Diameter of small end of land A = 103 — 105% final cable diameter
- Diameter of large end of land B = $2 \times$ diameter of small end, i.e. $2A$
- Length of land C = 10–12 times diameter of small end
i.e. $10-12A$.

These dies can be used with either adjustable or fixed centre heads but the long land tends to cause flowing back of polythene into the core tube unless wire is continually passing through the head while the extruder is running. A diagram of this type of die is given in Fig. 16.4.

For most operations, dies made of polished mild steel are quite satisfactory and are cheaper and easier to make than from a harder or tougher steel. When insulating steel conductors, however, the wear on the male die is quite considerable and can cause the conductor to become decentralized. For this operation tougher steels are commonly used, such as high carbon chrome alloy oil-hardened cast steel. Male dies having tips of tungsten carbide have been considered, but it is difficult to produce

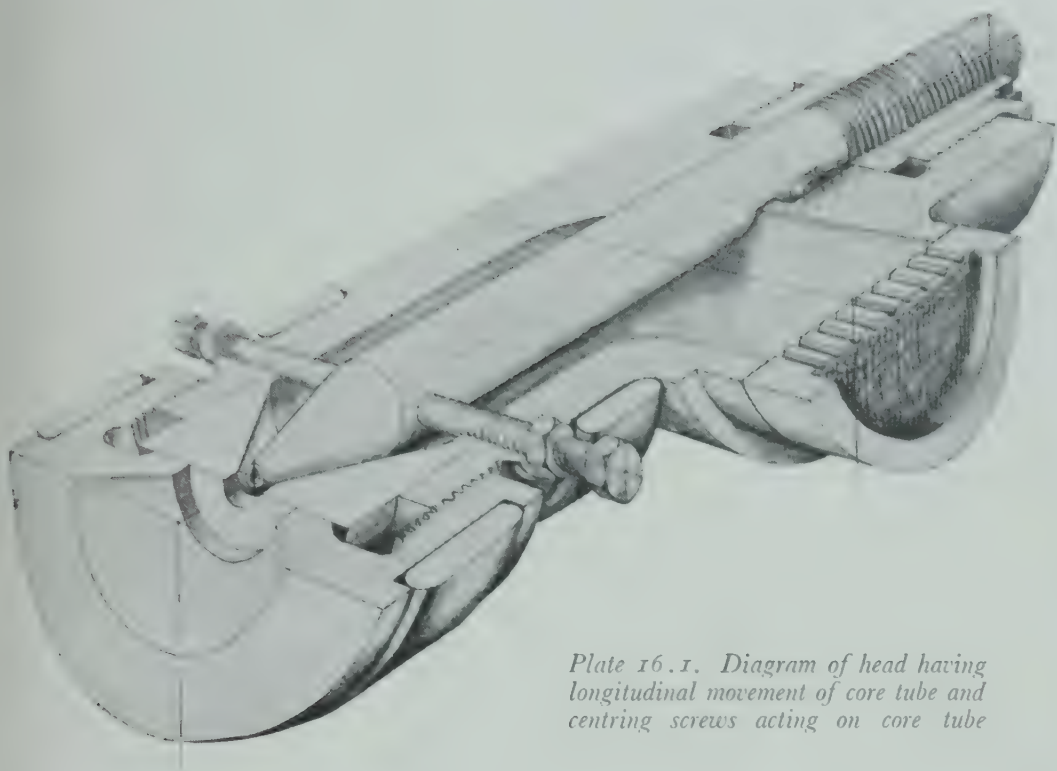


Plate 16.1. Diagram of head having longitudinal movement of core tube and centring screws acting on core tube

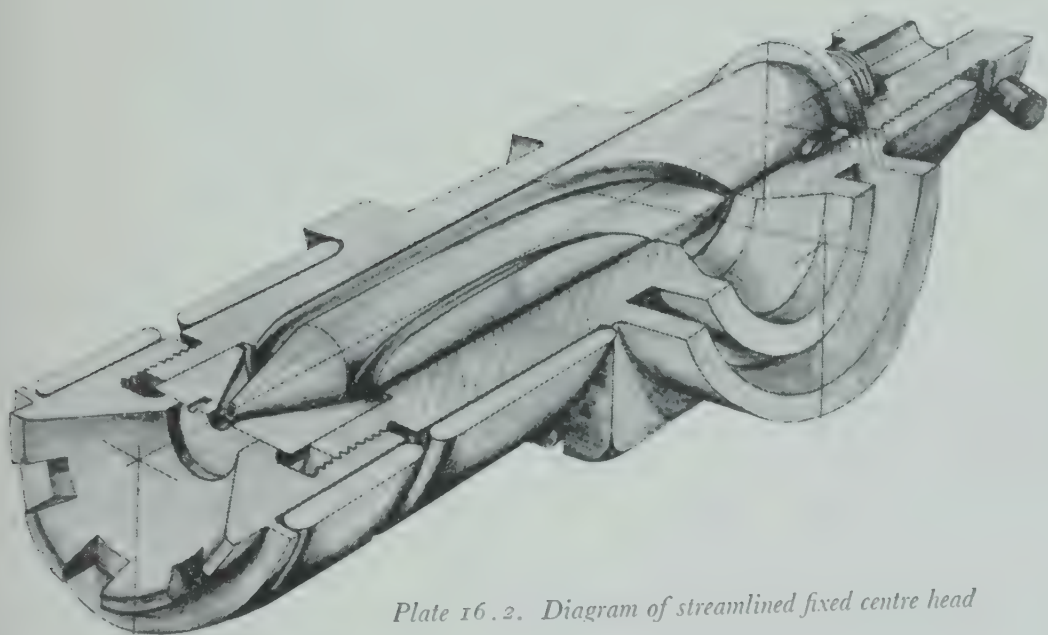


Plate 16.2. Diagram of streamlined fixed centre head

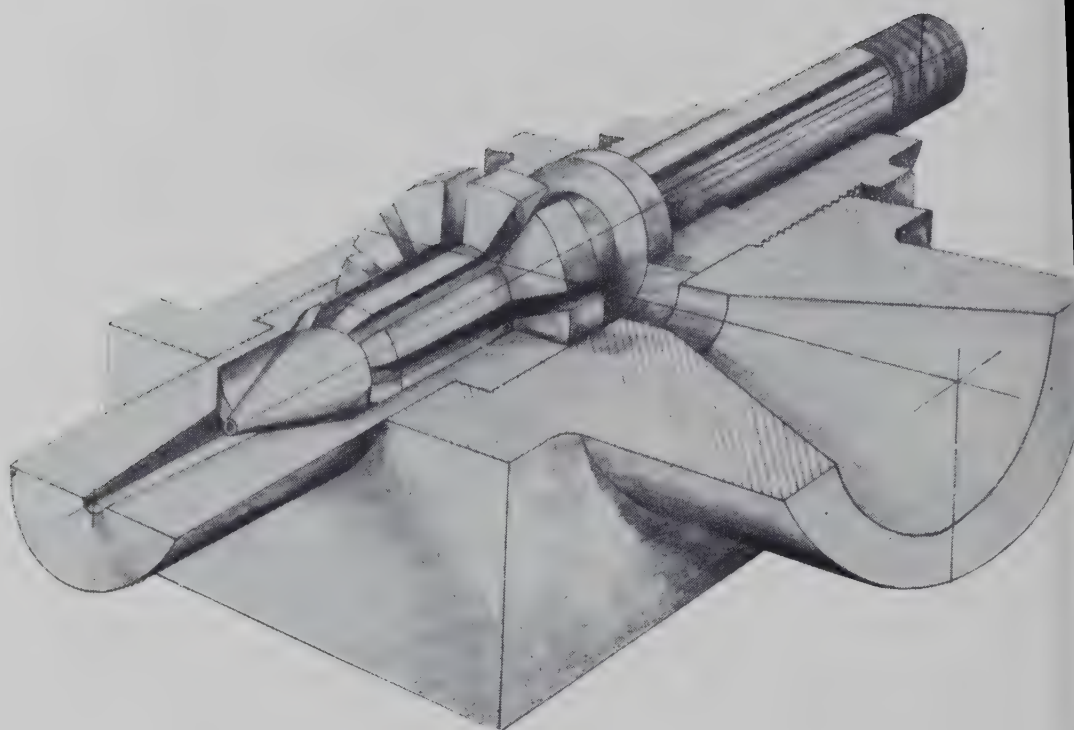


Plate 16 3. Diagram of simplified fixed centre head

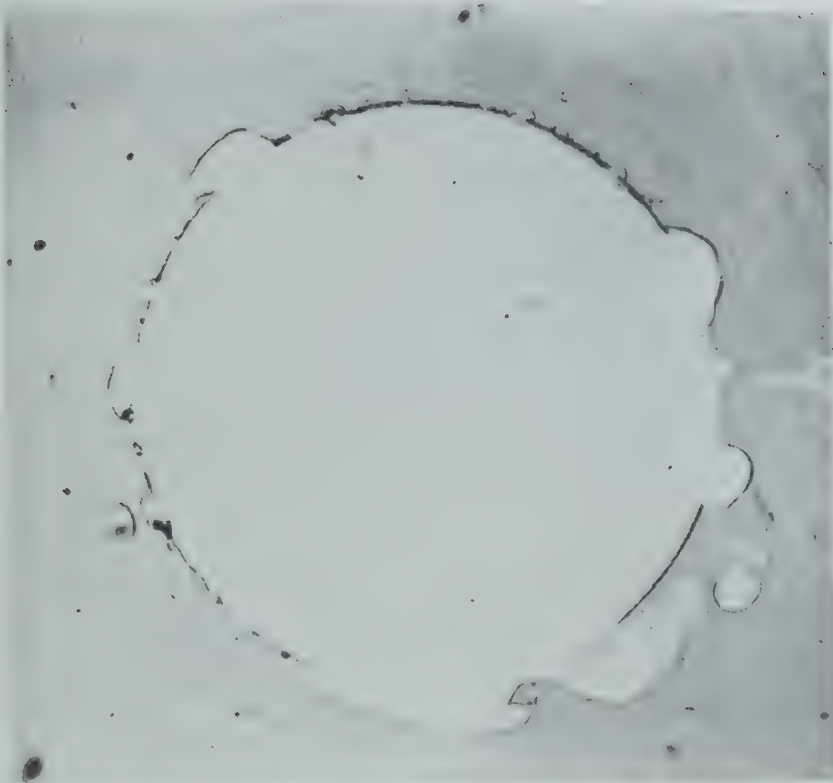


Plate 16.4. Section of polythene cable which has been rapidly cooled in cold water. Note voids around conductor

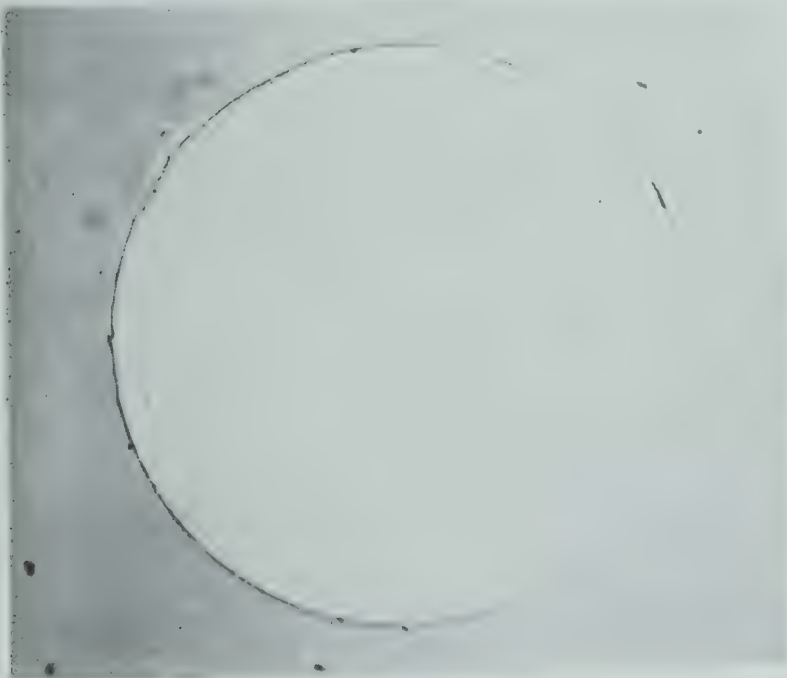


Plate 16.5. Section of polythene cable which has been correctly cooled. Note absence of voids



Plate 16.6. Longitudinal sections of polythene cable showing:

- | | |
|-----------------|---|
| <i>(Top)</i> | <i>Effect of quenching in cold water</i> |
| <i>(Centre)</i> | <i>Effect of too rapid cooling in hot water</i> |
| <i>(Bottom)</i> | <i>Effect of correct cooling in hot water</i> |

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the desired feather edge with this material because of its brittleness. For this reason, and because of the high cost of manufacture, these dies are not widely used, though they have excellent resistance to wear.

Dies should have a high polish on all surfaces, and should be made to very fine tolerances, particularly when used in a fixed centre head.

OPERATING TEMPERATURES

The operating temperatures for successful extrusion vary slightly from one machine to another, and depend on the melt index of the polythene to be extruded and the speed with which it passes along the scroll. In general, the lower the melt index and the faster the speed, the higher are the required machine temperatures.

The feed hopper must be kept cool, otherwise the granules tend to stick together; some machines have water cooled feed mouths specifically designed for this purpose. From the feed mouth the barrel is gradually raised in temperature to the delivery end, where the temperature is of the order of 200°C. The head is maintained at this temperature and the die is usually slightly higher. Typical values for various grades of polythene are given in Table 16.1.

Table 16.1. EXTRUDER TEMPERATURES FOR LOW DENSITY POLYTHENE

Melt index	Temperatures in °C						
	Feed mouth	Barrel			Head	Die	Extruded compound
		1	2	3			
20	below 50	120	140	160	160	170	160
7	" "	140	160	190	190	200	190
2	" "	160	200	240	240	250	240
0.2	" "	170	220	270	270	280	270

Machine temperatures are usually indicated by means of thermocouples placed in the barrel, head, and die, and hence the values recorded will depend on the characteristics of the machine and the exact positioning of the thermocouples. The practical point of importance is to extrude compound having the temperature shown in the last column of Table 16.1.

OUTPUT OF EXTRUDERS

The output of any extruder depends on a large number of variables, such as the characteristics and speed of the scroll, the wire mesh screens, size of die, etc., so that it is impossible to give accurate values for the output without knowing precise details of the machine in question.

In the cable industry, extruders with barrel diameters of $1\frac{1}{2}$ – $4\frac{1}{2}$ in. are commonly used. Usually the small machines are capable of higher scroll speeds; 80 rev/min is not uncommon for a $1\frac{1}{2}$ in. machine but it is unusual for a $3\frac{1}{4}$ in. machine to exceed 50 rev/min. It is not possible to quote definite figures, but the following values will give an indication of the

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output of various extruders. Up to 30 lb/hr can be expected from 1½ in., 35–40 lb/hr from a 2 in., 70–80 lb/hr from a 3 in. and 160 lb/hr from a 4½ in. machine.

In general it has been the practice to insulate small conductors 1½ in. or 2 in. machines but the present trend is to use larger machines in order to achieve higher linear speeds. When insulating small size conductors with relatively thin walls of polythene, linear speeds up to 700 ft/min are common using a 2 in. machine, but this can be increased to 1,500 ft/min and higher with say a 4½ in. machine. On the other hand, the linear speed is considerably reduced when extruding thick polythene coverings and may well be limited by the cooling time necessary to produce a void-free insulation. In such cases the speeds may be of the order of 10 ft/min.

COOLING

When the fluid polythene emerges from the extrusion die it is at a high temperature in the region of 200°C, and therefore must be cooled before it can be handled. The cooling bath must be very near to the die of the extruder as otherwise the polythene would tend to flow under gravity and give an eccentric covering.

The result of immersing a cable with a reasonable wall thickness of polythene at, say 200°C, into cold water is immediately to form a hard outside shell around the still fluid interior. As cooling gradually proceeds the volume of the polythene inside the hard shell decreases, and as the cohesion of polythene for itself is greater than for copper it shrinks away from the conductor towards the hard outer shell, leaving a series of cavities or voids around the conductor as illustrated in Plate 16.4.

The formation of such voids cannot be tolerated because of the serious effect on the electrical properties of the cable. The voids cause local irregularities of permittivity along the cable resulting in variations of characteristic impedance and consequent distortion of wave transmission, particularly if the voids are regularly spaced. Freedom from voids is essential when the dielectric is to be subjected to high voltage. In this case the voids are potential sources of ionization, which can result in rapid electrical breakdown.

It is possible to extrude thin walls of polythene up to about 0.025 in. followed by cold water quenching, without the formation of voids. Many radio frequency cables require wall thicknesses much greater than this and, if cold water quenching is used, it is necessary to extrude the polythene in a number of thin layers to achieve a substantially void-free dielectric. There are several disadvantages of this method, such as the difficulty of achieving concentricity and the lack of bonding between successive layers of polythene.

Apart from the technical objections to the multi-layer extrusion method the process is relatively uneconomical as it involves much handling of cable, and the general trend has been to develop cooling processes which would enable thick walls to be extruded in one application.

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For example, in one method the extruded polythene covering was cooled in three distinct zones of different temperatures. The first zone was maintained at a temperature just above the solidification point of polythene, at about 110°C , and the cable was immersed in this zone long enough for the whole of the polythene to have fallen substantially to this temperature. Up to this stage there was no tendency to form voids since the whole of the polythene remained plastic, yet a large proportion of the total density change had taken place. The cable was next passed into a zone at $95\text{--}100^{\circ}\text{C}$, at which temperature the polythene became substantially solidified, and finally the cable was immersed in cold water to complete the cooling process. The provision of a convenient coolant at 110°C presented some problems; one solution adopted was to use water above atmospheric pressure. The cooling bath consisted of a tube, coupled directly on to the extruder, through which water was pumped under pressure in a direction opposite to that of the extruded cable. Electric heaters provided the necessary temperature control, and the pressure in the tube was maintained by a simple rubber gland at the outlet end. The time required to cool the cable in each zone was calculated from the thermal properties of polythene and the dimensions of the cable, and hence the speed of the cable through the graded cooling tube could be determined. Using this method, void-free cable having wall thicknesses up to about 0.2 in. were obtained with melt index 7 polythene, though the speed of cable was very slow in comparison with previous techniques. The limit of 0.2 in. was fixed only by the dimensions of the tube. As an example of the necessary cooling times, a cable having a conductor of 0.052 in. and overall diameter about 0.300 in. had to remain in each cooling zone for about 25–30 sec. Thus for a cooling tube 30 ft. long the speed was restricted to 20–24 ft/min. A photograph of a section of a cable produced in this way is reproduced in Plate 16.5.

The technique of graded cooling described above, while quite successful, was never popular partly because of the rather elaborate equipment needed, but the results gave a strong indication of cooling times and temperatures required, and later it became evident that it was possible to dispense with the hottest of the three zones and to take the cable straight into the zone at $95\text{--}100^{\circ}\text{C}$. This allowed much simplification of the process as hot water in an open trough could be used as the coolant. By this method, with immersion times in the hot zone of up to 10 mins, wall thicknesses of up to 0.3 in. have been successfully applied without void formation. Cooling times of this duration require very long troughs unless production speeds are to be prohibitively slow, and a suitable length of trough for large cables is about 100 ft. The weight of such a length of cable, even in water, is considerable, and hence the trough must be made fairly deep to accommodate the sag in the catenary, a depth of 2 ft.–2 ft. 6 in. being sufficient for a 100 ft. trough. The water in the trough can conveniently be heated by injecting steam at frequent intervals along the first 70 ft. from the extruder end. The last 30 ft. of the trough is left cold, and this is achieved by inserting a baffle about two-

thirds of the way along the trough and feeding in cold water at this point, at the same time compensating for losses of water from the trough ends.

There is some evidence that it is possibly easier to produce void-free cable using harder grades, such as melt index 2 and 0.2, than for melt index 7 and 20, the latter grades requiring slightly longer periods in the hot zone. While calculations give a rough guide as to the cooling time to be allowed, it is preferable to determine the shortest time for any given cable empirically, by running the cable through the bath at increasing speeds until voids appear. The best way of detecting voids is to slice at least 12 in. of insulation from the cable longitudinally and examine the groove left by the conductor. Any voids present, which may be several inches apart, will appear next to the conductor, and can usually be seen with the unaided eye. There is a difference between voids produced by immersing cable in cold water and by immersing it for too short a time in hot water. In the first case there are very many small voids, and the groove left by the conductor is matt in appearance. Voids produced by incorrect cooling in hot water are much larger, usually at least 0.010 in. in diameter, and are spaced at irregular intervals along the groove, which is smooth and shiny. Various types of void formations are shown in Plate 16.6.

INPUT STAND

The drum of conductor or core to be covered is mounted on the input stand behind the extruder. Little need be said of this item, except that it is essential that the conductor should pay out smoothly without over-running. To achieve this the drum is often fitted with a simple friction brake. This method has the disadvantage that the tension increases as the amount of conductor on the drum decreases, and stands are available in which the tension is continually adjusted throughout the run. The general feature of such equipment is that the conductor is taken over a pulley on a spring loaded arm, the movement of which adjusts the pressure on the friction pads of the braking mechanism. More elaborate arrangements employing a tension control stand and driven input drum exist.

CAPSTAN WHEEL

The prime purpose of the capstan wheel is to pull the conductor at uniform speed through the head, the quality of the cable produced depending very largely on the smoothness and constancy of this drive. Adjustment of the speed of the capstan wheel is often a convenient way of controlling the cable size, although the difference between the dimensions of the die and finished cable should not be greater than 10%.

In cables for use at high frequencies, it is essential that the diameter should be controlled within very close limits and uniformity of the speed of the capstan wheel is very important in obtaining this control. Any irregularity in the speed of the capstan means that the speed of the conductor through the head is not constant, resulting in diameter varia-

on of the extruded covering. Diameter variations of the cable cause local variations of the characteristic impedance which result in undesirable distortion of wave transmission.

The dimensions of the capstan wheel depend on the size of cable to be made but it is usually between 2 ft. and 3 ft. in diameter. It is often convenient to make the circumference of the wheel a whole number of feet or yards, as a revolution counter suitably geared will then provide a useful check on the length of cable run. The capstan wheel is usually about 6 in. wide to enable the cable to be taken several times around it to prevent slipping.

The method of driving the capstan wheel should be selected carefully. Experience has shown that the presence of spur gears in the driving mechanism, unless these are of very good quality, is undesirable, as their meshing can cause a slight pulsation at the periphery of the capstan wheel which results in diameter variations on the cable. The modern tendency is to eliminate spur gears as far as possible and to use only worm reduction gearing. It may be necessary in some cases to use spur gears as alternative matched pairs to give different speed ranges. If this is the case, they must be arranged at the high speed end of the gear train, where their pulsations will be least detectable.

The capstan should be capable of a wide range of speed adjustment, which may be obtained by the use of a variable speed motor in conjunction with change gears, positive infinitely variable gears, or variable hydraulic gears.

While the use of a single capstan wheel gives a sufficiently smooth drive for most purposes, the best result can be obtained by using two capstan wheels, one before the extruder and one after the cooling trough, the cable running between them under slight tension. In such an arrangement the two wheels are driven at the same speed and are of approximately the same diameter. Some provision must be made for relative adjustments of the speeds of these wheels to allow for the fact that when the polythene covering is applied, an increase in diameter results, and when wound around the second capstan wheel, the increase in size will have the same effect as a slight increase of diameter of the wheel, resulting in an increased tension on the cable. This can be compensated by making one of the wheels, usually that behind the extruder, either slightly conical or stepped, each step being about 0.050 in. deep and $1\frac{1}{2}$ –2 in. wide. Provision is made for the wheel to be moved along its axis so that the correct position can be selected to give the required slight tension in the cable between the two wheels. Using this system any jerking of the input drum or the final take-up drum cannot cause local irregularities in the extrusion.

Large cables cannot be handled satisfactorily by capstan wheels, unless the wheels are very large in diameter. A more convenient way of pulling these cables through the extruder is to use a capstan wheel behind the extruder for metering in the conductor at constant speed, and to drag the covered cable with a caterpillar haul-off pulling at constant tension.

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TAKE-UP STANDS

The main requirement of the take-up stand is that it should wind cable on to the output drum, adjusting the speed of the drum to compensate for the building up of diameter as the drum fills up. The simple method is to drive the drum through a slipping clutch. This has the disadvantage that the tension of the cable decreases as the drum fills and sometimes means that the tension on the inner layers has to be greater than is desirable if the clutch is to drive the drum at all when it is full of heavy cable. For many cables this method is satisfactory, but it is apt to give trouble particularly on small cables with fine wire conductors.

To overcome this problem, take-up stands have been designed which wind up the cable under constant tension. The usual way in which this is accomplished is to employ a control frame on which is mounted a sliding pulley. The cable is run through the control frame and a loop is made to support the sliding pulley, which may be loaded with additional weights to give the required tension to the cable. When the take-up drum is winding at the correct tension there is no movement of the pulley, but increase in winding tension causes the pulley to move upward and vice versa. The movement of the pulley can be employed to operate a simple control mechanism operating on compressed air or electricity which makes a suitable adjustment to correct the tension. In some stands the adjustment is made to the pressure of a continually slipping clutch while on others the drum is always positively driven, the speed being adjusted by the control gear.

For long runs, stands equipped with two drums are available thereby permitting change over from one drum to the other without pause in the extrusion process.

DETECTION OF INSULATION FAULTS

When extruding thin walls of polythene, a small foreign body, such as a piece of grit, may accidentally find its way into the feed pocket and possibly past the screen pack and on to the cable causing an incipient electrical fault or even a complete break in the insulation. Weak spots can also be caused by sudden jerks on the conductor, poor centralization of the conductor, or possibly by bad dispersion of carbon black in the polythene. It is convenient that these faults should be detected immediately after extrusion and before the cable is wound up, this being done by the spark tester.

In one fault detector the insulated core is passed through an electrode consisting of a tunnel about 2 ft. long, from the roof of which hang a large number of flexible chains which are maintained at a high voltage and so arranged that the cable in passing through must brush against many of them. The test voltage applied to the electrode is usually between 3 and 12 kV according to the thickness of the dielectric. The conductor of the cable is earthed so that any weak spots or holes in the polythene allow the high potential to discharge to earth, the small discharge current

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activating a system of relays which in turn operates a warning device such as a bell or light. In some spark testers these relays have to be reset manually, but others reset themselves after a short interval and also operate a counter indicating the total number of faults.

DIAMETER GAUGES AND CONTROLLERS

It is important that the diameter of the extruded cable should be accurately controlled, and this can be done on the moving cable by measuring the diameter at frequent intervals and making any adjustments to the speed of the capstan wheel manually. With good equipment, once the plant has been set up, there is little variation, but some factors remain unpredictable, as for example the fluctuation of supply voltage and the progressive clogging of the screens, and it is convenient to have an automatic measuring device so that any changes can be immediately registered and corrected.

Diameter gauges are of two main types, optical and mechanical. The optical types usually work on the principle that light from a uniform source is split into two beams, each of which is focussed on the same photo-electric cell. The cable to be measured passes through one of these beams, so cutting off a proportion of the light to the cell, and the amount of light from the other beam is adjusted to the same value either by placing a rod of the same size as the cable in this beam or by reducing the total area of the beam by adjustable slits. An interrupter is arranged in the beams so that light from each falls on the cell alternately. When the cable is the correct size, the d.c. output from the cell is constant but variations in cable size cause variations in this output. This takes the form of a square wave of the same frequency as the interrupter, and by suitable electronic equipment the amplitude of this wave can be made to indicate the magnitude of the change of cable size, or adjust the speed of the capstan wheel to correct it.

In mechanical gauges the cable is passed between two rollers or between a skid and a roller. Diameter variations cause movement of the skid or roller and this movement can be used in a variety of ways. The simplest device is to arrange electrical contacts at a pre-determined distance away from the zero position, so that when the cable varies by more than this distance in either direction the appropriate contact is closed and can be made to operate a warning light or adjust the speed of the capstan wheel. Another type of gauge uses the movement of the skid to alter the position of a soft iron core in a solenoid which causes unbalance in a bridge circuit, the unbalance current being indicated on a meter calibrated direct in units of 0.001 in., or used to operate a speed control system.

ECCENTRICITY GAUGES

In addition to accurate control of diameter, many cables require that the conductor shall be accurately centralized in the polythene insulation, and this is particularly true for radio and television relay quad cables.

These cables have four polythene insulated conductors laid up together and a polythene sheath overall, and it is essential for satisfactory operation that the capacity between the various pairs of conductors is precisely controlled. To achieve this the geometrical spacing of the conductors must be constant along the whole length of the cable, and this can only be achieved if the diameter of each core is constant and the conductors concentric within very close limits.

If a fixed centre head is used, the centralization of the conductors is ensured by the design of the head. When using adjustable heads, the dies are first positioned roughly by eye and the final adjustments made by suitably altering the relative positions of the dies after examining cross sections of the cable produced. This method may take a considerable time, causing waste of material, and leaves no safeguard against possible disturbance of the adjustment during the run.

To overcome these drawbacks several devices have been designed and patented which indicate the degree of eccentricity of the conductors while the cable is running. One method employs the principle that the variation of electro-magnetic flux through a coil of wire causes an induced e.m.f. in the coil. The cable is run between the poles of an electro-magnet energized by alternating current. A strip of conducting material, known as the gauge conductor, is spring loaded against the cable parallel to the conductor so that the plane defined by the gauge conductor and the conductor of the cable is at right angles to the magnetic field of the electro-magnet. If these two conductors are connected to form a loop, any variation in the magnitude of the magnetic field linking this loop will result in a corresponding change in the e.m.f. induced in it. The magnitude of this induced e.m.f. depends, amongst other things, on the area enclosed by the loop within the field of the electro-magnet. Since the gauge conductor extends beyond the magnetic field the effective area of the loop depends on the distance apart of the gauge conductor and the conductor of the cable, and hence the magnitude of the induced e.m.f. also depends on this distance. If a similar gauge conductor is placed on the opposite side of the cable, and the two circuits arranged so that the induced e.m.f.s. are opposing, the resultant e.m.f. indicates any difference between the distance apart of the conductor and the two gauge conductors. When the conductor is exactly midway between the gauge conductors, the resultant e.m.f. is zero. A second pair of gauge conductors arranged at right angles to the first pair, will give the eccentricity in this plane, and the vectorial sum of the two resultants gives the total amount of eccentricity of the conductor. This can conveniently be indicated on a cathode ray tube, when the deflection of the spot from the centre of the screen gives a direct indication of the magnitude and direction of the eccentricity present.

A variation of this method is to interchange the roles of the electro-magnet and the loop of wire formed by the gauge conductor and the conductor of the cable, and to inject an alternating current into the loop and measure the induced e.m.f. in the coil of the electro-magnet.

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Another type of eccentricity gauge employs X-rays to allow direct examination of the position of the conductor in the dielectric. A slit source of X-rays is placed close to and parallel to the cable and the X-ray picture of the cable is examined on a fluorescent screen arranged some distance from the cable so that the image of the cable is magnified to about 10 times the original. The wavelength and intensity of the X-rays are arranged so that the conductor appears quite dark and the polythene as a half tone. The apparatus can be rotated through 90° so that the cable can be viewed in two directions at right angles. The X-ray tube has a fairly short operating life and is quite expensive to replace, so that the gauge can only be used intermittently, but this should not be a very serious drawback in service.

POLYTHENE COMPOSITION FOR EXTRUSION

Having considered the most suitable equipment for the production of polythene cables, it is desirable to review briefly the special compounding of the polythene composition in order that it may be suitable for use as a dielectric or sheathing material for cables.

In general, the harder and higher molecular weight polythenes are most satisfactory for cable work on account of their improved resistance to low temperatures and environmental cracking in service. The present trend is to use preferably melt index 2 or alternatively melt index 7 for general purposes and the harder melt index 0.2 for cables where the highest order of quality is required.

To ensure that the excellent properties, especially the power factor, of polythene are not impaired by the extrusion process it is necessary to incorporate antioxidants in the material. Suitable antioxidants* are di-*o*-cresylol propane for compounds other than black in colour, and di- β -naphthyl-*p*-phenylene diamine where the staining effect of this material is not important. Usually 0.1% of either of these materials gives satisfactory results. The antioxidant is commonly supplied as a masterbatch in granular form and can be mixed with the polythene granules by a simple tumbling process and this mixture is then fed directly to the extruder. If the hot feeding technique is in use, the antioxidant is added on the mill. This is necessary as there is a fairly rapid deterioration of the polythene on the mill if no antioxidant is used. As well as preventing oxidation during processing, the addition of antioxidant helps to ensure a satisfactory performance when the cable is exposed to heat in service.

Very considerable quantities of polythene insulated and sheathed cables are now in operation for radio and television relay systems where they may be exposed to sunlight. In such cases it is essential to incorporate about 2% of fine particle carbon black in the sheathing compound to prevent cracking of the polythene by the photo-catalytic action of the ultra-violet rays. Carbon black is normally added in the form of a polythene masterbatch in which either 10% or 30% black is very well dispersed. For best results this should be mixed with the polythene in

* See Chapter 6

the correct proportions, either in an internal mixer or on an open mill, both these methods yielding sufficiently good dispersion. The alternative method of tumbling the granules of master-batch with those of the polythene and feeding the mixture to the extruders is often used, but requires very careful control to ensure satisfactory dispersion, not only depending on the efficiency of the tumbling and the mixing effect of the extruder scroll.

Where coloured compounds are required, the compounding follows conventional practice. To maintain the electrical properties of polythene the smallest amount of colour consistent with positive identification should be used, particularly when using carbon black for colouring cable insulation.

In the early days of polythene extrusion, when equipment was not so good as it is today, it was found that the addition of a small proportion of polyisobutylene afforded easier processing and improved the low temperature performance of the soft grades of polythene then in use. Today this is not necessary with melt index 7 and 2, but addition of 5% polyisobutylene does assist in extruding melt index 0.2. The mixing can be done on an open mill, the procedure being to masticate the polyisobutylene thoroughly, and then to add the polythene gradually. An attempt to reverse this order and add polyisobutylene to polythene, will probably result in a poor dispersion. There is some evidence that the addition of polyisobutylene to some types of polythene improves the resistance of the cable to environmental cracking.

A recent development in the field of polythene cables has been the introduction of cellular or expanded polythene. The method of producing the cellular material is to incorporate in the polythene an organic material which will decompose and liberate a gas, usually nitrogen, at a temperature just below the extrusion temperature of polythene. Two suitable materials are *p,p'*-oxy-bis-benzene-sulphonhydrazide and azo-di-carbonamide. The blowing agents are usually powders and may be tumbled with the polythene granules in the correct proportions and fed as a mixture to the extruder. Better methods are to add the blowing agent to polythene either on an open mill or in an internal mixer at a temperature below the decomposition point and to regranulate the compound.

When this material is fed into the extruder, the blowing agent decomposes in the machine, but the gas produced cannot expand because of the high pressure in the barrel and head. On emerging from the die the external pressure is released and the expansion of the gas gives the polythene a cellular structure. The degree of expansion can be controlled by the amount of blowing agent used and by the time available for expansion before the material is quenched. Water troughs, whose distance from the die can be adjusted, are very helpful for this purpose. Expansions of about 2 to 1 are common, the resulting material having a specific gravity of about 0.45 and a permittivity of about 1.5. The size of the die should be chosen so that the area of the aperture is approximately half that of the desired cable. The extrusion temperatures and

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amount of blowing agent required depend, of course, on the actual blowing agent being used, but normally about 1% of the more common types is sufficient.

Cellular polythene has applications in the radio frequency field, a popular application being the insulation of television aerial downleads. It is possible that the material may prove suitable for the insulation of telephone cables and in this application the uniformity of the cellular structure and the control of dimensions are most important requirements.

Another recent development has been the introduction of high density polythene. This material, with its higher melting point and much greater toughness and rigidity than conventional polythene, offers obvious scope for utilization in electric cables. Information in regard to the processing, however, is limited. The high extrusion temperatures and the relatively poor flow properties of the material have presented new problems in the production of close-fitting void-free cable insulants and at the present stage of development it is not possible to specify extrusion conditions with any degree of confidence. There is also need for further study of the efficacy of the available antioxidants. The indications are, however, that modifications in extrusion technique will overcome the processing difficulties and that conventional modern extrusion equipment will prove suitable for handling this material.

CONCLUSION

Since the introduction of polythene the number of applications in the field of electric cables has steadily grown due to developments in extrusion technique. It seems reasonable to think that further extension of the range of cables, particularly those for telecommunications and high voltage power distribution, will depend largely on the skill of the cable maker. Interesting possibilities for the future are offered by the development of cellular polythene, the process of crosslinking by electron bombardment* and the emergence of high density polythene.

* See Chapter 13.

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CHAPTER 17

THE EXTRUSION OF TUBE, ROD AND PROFILE

E. G. FISHER

IN general terms, the manufacture of tubes, rods and profiles in polythene can be briefly and simply stated as follows: polythene in chip, granules or other convenient form, is fed continuously to the revolving screw or screws of a suitably adjusted extrusion machine and is thereby converted into an homogeneous melt under pressure. It is forced through a screen pack breaker plate system, and thence to the extrusion die orifice where it is given form and dimensions convenient for shaping and sizing whilst still molten, into the final form of the finished product.

After the material leaves the extrusion die, it is drawn under controlled tension, by a take-off system of suitable type, into and through a cooled forming device where the product is continuously sized and set to the required form.

The forming operation is followed by further controlled cooling and the finished product passes to the wind-up, cut-off device or other finished product handling system.

The complete process as outlined above, may be modified in the case of certain relatively simple products when separate sizing or forming devices are unnecessary. In these cases—polythene capillary tubes, strips of small dimensions and polythene flat film may be cited as examples—controlled tension or draw-down, and final cooling only is needed to give dimensional control, and to preserve the simple form of the product.

THE EXTRUSION MACHINE

Polythene appears to be one of the easiest thermoplastics to handle in an extrusion machine. It flows very well, shows little apparent tendency to stagnate in poorly streamlined parts of the equipment, and does not noticeably decompose or oxidize until quite serious overheating or other mishandling has taken place. Furthermore, the physical properties of the material make it very suitable for the shearing action of a screw extruder and thus for the generation of work heat in the polymer.

Any screw extrusion machine, therefore, which has been designed for thermoplastic material, and which is known to give a good melt, can be used with varying degrees of success for the extrusion of polythene tubes, rods and profiles.

The main criticism of such machinery, which is usually fitted with what may be called general purpose screws, is concerned with questions

of quantity, and in recent years there has been considerable research into the mechanism of the extrusion process in order to increase output.

This work and its results, have been treated in considerable detail in a previous chapter* and elsewhere,^{1, 2, 3, 4} and little further comment is therefore, necessary here. There are, however, certain other aspects of the modern theory of extrusion which greatly concern the users of existing machines.

Although, as has been previously stated, the extrusion of polythene at comparatively low output rates for extrusion machine size is a rather simple matter, the production of a good extrudate at high speed becomes quite difficult. To produce the required homogeneous melt, it is necessary to supply heat uniformly to the polythene during the time it is in the barrel of the extrusion machine. It is usual to supply heat in two ways, i.e. by conduction from the heated walls of the barrel, or by mechanical work by friction deformation and shear of the polythene.

The former method uses the heat developed in electrical resistance heaters situated on the outside of the barrel of the machine, or transferred to the barrel by some means such as heated oil, etc. The latter method functions by the conversion of part of the horse power of the drive motor into heat energy. Existing extrusion machines utilize a varying proportion of these two heat sources, depending on the characteristics of the screw, the melt properties and viscosity of the thermoplastic, and the general design of the extrusion machine. Heat by conduction from the barrel tends to give a heat gradient radially in the polymer, and thus does not so readily give an homogeneous melt. Mechanical working however, causes the development of heat actually within the material and, therefore, can be expected to give a more uniform product. This fact has been appreciated for many years by extruders of plasticized vinyls as the viscosity characteristics of that material enables them to dispense almost entirely with conducted heat, except during the start-up period.

Another important difference between the two methods of heating, is that, whereas with conducted heat the melt capacity, and thus the output of the machine, is limited by the contact area of the barrel, the limitation with frictional heat exists only in the power and mechanical efficiency of the drive.

Adiabatic working

Recent trends therefore, in the theory of extrusion machine design for polythene, have been prompted by the above considerations to suggest that the ideal machine for the extrusion of this thermoplastic, should work under near adiabatic conditions where all, or nearly all, the required heat is given by mechanical work.

Such a machine has a high compression ratio screw capable of efficient shear, extremely rugged thrust race and reduction gear assembly etc.; and

* See Chapter 15.

a drive motor of adequate horse power. The screw is geared to operate at high speeds, i.e. up to 200 rev./min or more, and some controllable valving arrangement is necessary to ensure the required mechanical work at lower output. The screw L/D ratio is not particularly important.

There are still authorities who do not agree with the above concept of an ideal polythene extrusion machine. This difference of opinion is based largely on economic considerations. The advocates of this opposite view, whom it must be admitted have some grounds for their opinion, state that an extrusion machine which uses a higher proportion of conducted heat, can be lighter in construction and more easily serviced and maintained, and therefore, more cheaply constructed and economical to run. It can also be said that heating by means of static heaters is cheaper, trouble-free, and more easily controlled; and more economical because it is not influenced by mechanical inefficiencies.⁵

In support of these views it is stated that, although adiabatic working should, and does, give a homogeneous melt, the product obtained in practice when a higher proportion of conducted heat is used under the correct conditions, can be equally good because of the screw mixing action.

An extrusion machine constructed according to these views would follow the more normal lines, but would have a high L/D ratio—at least 15 : 1 in order to give ample contact area for heat conduction.

The types of extruder which give most support to the latter theory, are the various makes of multi-screw machines. In these, the mechanical working by shear is reduced to a minimum and a high proportion of the required heat is given by conduction. But, in spite of this, good outputs of homogeneous polythene melts may be obtained from such machines when they are correctly used.

It has been shown that, in a normal machine, the two systems of heating are used together in varying proportions, depending on the characteristics of the machine, and on other variables. The possible maximum output from the machine may be increased in two ways, i.e. by increasing the length of the screw and barrel in order to give greater contact area for the conducted heat; and by increasing the screw revolutions and pressure, so that more work is put into the material. The homogeneity of the melt, and thus the quality of the product, may be improved by increasing the mechanical work and the mixing action of the screw on the material. In practice this would be carried out by increasing the compression ratio of the screw, by increasing the restriction of the die screen pack system, by reducing the barrel/polymer temperature gradient or by means of a combination of all of these. If the latter method is used, then the L/D ratio must be adequate so that the total quantity of conducted heat is not reduced.

In contemplating the purchase and installation of a new machine for the extrusion of polythene products generally, it is possible nowadays, in the writer's experience, to go some way towards securing the "best of both worlds," bearing in mind the considerations contained in the previous

paragraph. And for this, the machine should have approximate following specifications.

Screw

Constant pitch, decreasing depth with definite feed, compression melt zones. Melt zone to occupy about 30% of effective screw length. Helix angle 18° to 25° single start. L/D ratio to be at least 15 : 1. Compression ratio at least 3 : 1. Screw to be finished with a conical nose and to be bored for water cooling for its entire length. As a compression ratio of 5 : 1 or more has been found to give some advantage with film products, to be described later, provision for easy interchangeability should be made.

Drive

The important features here are the h.p. of the motor and the maximum rev/min of the screw. The following can be given as an indication of minimum requirements in extrusion machines of various sizes:

$1\frac{1}{4}$ in. screw diameter—	5 h.p.	120 rev/min	} continuously variable
$2\frac{1}{2}$ in. " "	—15 "	100 "	
$4\frac{1}{2}$ in. " "	—50 "	80 "	

Barrel

Again, the important feature is the maximum loading of the heating elements with which to provide conducted heat. As an example:

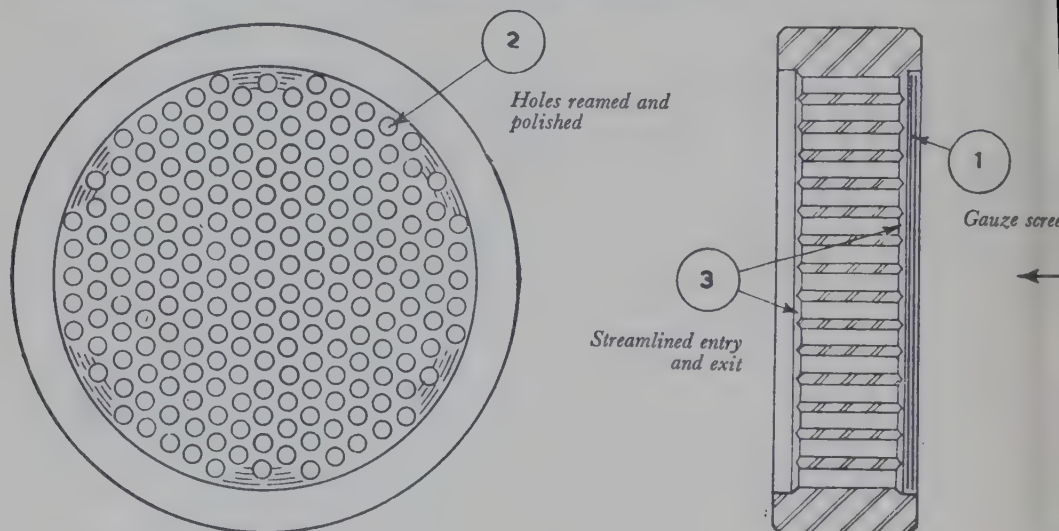


Fig. 17.1. Breaker plate, showing screen pack

can be stated that a $2\frac{1}{2}$ in. machine, in order to obtain the "best of both worlds", should have a minimum total loading of about 12 kW on the barrel.

An extrusion machine designed according to the above specification and with adequate construction details, should be capable of delivering between 7 and 8 lb. of homogeneous polythene melt per horse power of the drive motor. Such machines are already available.

An important part of the extrusion machine, which has a considerable effect on the correct functioning of the screw and heating system, is the

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breaker plate screen pack assembly. (Fig. 17.1.) Theoretically, if the screw and heating systems generally have been designed correctly to suit the characteristics of the die and the viscosity of the material at extruding temperature, then the screen pack should be just fine enough to filter the material only. In practice, however, extrusion machines are never like this. They have to be designed in a compromise manner, so that many jobs can be tackled without time consuming changes. This means that the compression ratio of the screw usually is lower than would be ideal on most polythene extrusion work; and consequently, would not give an homogeneous melt unless some other method of increasing the pressure gradient were available.

One method of doing this is to increase the degree of water cooling on the screw. But, in addition to this, the most effective way of controlling the pressure gradient in practice, is to increase or decrease the number and fineness of the gauze screens, which constitute the screen pack. By this means it is possible to carry out excellent polythene extrusions on machines which would otherwise be considered unsuitable, and it will be useful at this stage to tabulate a number of filter systems suited to the machines of various types (Table 17.1).

Table 17.1. FILTER SYSTEMS FOR VARIOUS EXTRUSION MACHINES

Machine type	Screen pack	
	Average tube, rod and profile	Large tube or profile of big cross-section
Long screw; high compression ratio: (4 : 1 and above)	2 × 60 mesh	60—100—60—mesh
Long screw, low compression ratio: (3 : 1 or less)	60—100—60 mesh	60—100—100—60 mesh
Short screw (12 L/D and less) and low compression	60—100—100—60	60—100—200—100—60
Twin-screw: Windsor type	60—100—200—100—60	60—100—200—100—60
Twin-screw: Trudex type	60—100—100—60	60—100—100—100—60

All screen pack systems to be supported on a 20-mesh gauze, placed next to the breaker plate which may consist of a disc of stainless steel perforated with a large number of reamed, polished $\frac{1}{8}$ in. to $\frac{1}{4}$ in. holes to take up approximately half the total area of the plate. As an example of this type of construction a breaker plate from a well known make of 3 in. machine contains 174 carefully spaced holes of $\frac{5}{16}$ in. diameter in a disc of $\frac{1}{4}$ in. thickness. (Fig. 17.1.)

The gauze combinations in Table 17.1 are given as a result of practical experience with the various types of machine. It must be remembered

however, that machines vary very much, and the screen pack which suited to one, will not necessarily be correct for another supposed similar machine.

The guiding principle should be to use the lightest pack which give an homogeneous melt, having regard to the extrusion die restriction and the throughput rate of polythene.

HIGH DENSITY POLYTHENE

The foregoing remarks and data are based on the normal low density polythenes made by the high pressure process. These materials have been commercially available for a number of years, and a substantial background of practical extrusion experience has been built up around them. Thus, it is possible to give details of the various techniques in the certain knowledge that they have been used with success for many years.

The high density polythenes exhibit certain different properties: they are harder, show improved strength and increased heat resistance, and may, in consequence, become important materials for extrusion in pipes, rods and profiles. Due to the very limited period during which the high density polythenes have been available in other than small experimental quantities, there is as yet, no dependable background of practical extrusion experience. It is not possible at this time, therefore, to describe the extrusion behaviour of the new materials with the same certainty as is possible with the long established low density polythenes.

The most important characteristic from the point of view of extrusion is that the high density materials are harder and develop high pressure in the equipment. This is, of course, to be expected in view of the increased molecular weights and consequent higher melt viscosities; the difficulties due to this effect do, in fact, increase as these values go up.

As a guide, it can be said that the high density polythenes, and in particular the high and very high molecular weight varieties, behave in the extrusion machine in much the same manner as unplasticized p.v.c.—apart, of course, from the question of thermal stability. This similarity is strengthened by the fact that some of the materials are available in the form of powder from which state rigid p.v.c. is also frequently extruded.

From the point of view of the extrusion machine, and in consequence of the higher melt viscosity, it is likely that the following changes will be required for the new materials:—

1. *Screw.* This will be more deeply cut; of lower compression ratio, i.e. 2 : 1 or thereabouts; and will have a shorter melt zone if any. Little or no water cooling is required.

2. *Drive.* The drive requirements are greater, so that the horse power of the motor will be higher and the reduction gear and thrust race arrangements sufficiently robust. Screw speeds are generally lower, as are outputs at the present time.

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3. *Barrel.* No work has yet been done on the application of high density polythenes to near adiabatic working. It is thought, however, that they should lend themselves very well to this technique, provided the extrusion machine is of sufficiently robust construction. For normal working the barrel heaters must be powerful enough to raise the material to the required temperatures, which are approximately 25°C – 30°C higher throughout, than those applicable to low density materials.

4. *Screen pack.* In the writer's experience, it is only possible to use coarse screens with the new materials because of the very high pressures which so easily develop and the consequent strain on the equipment. Provided the material is clean however, this is obviously of little importance under these circumstances.

5. *Extrusion conditions.* Suggested extrusion conditions for high density polythene of molecular weight 100,000, are as follows.

	<i>Temperature °C</i>
Barrel	150
„	160
„	170
Head	190
Die	195–220
Screen Pack	<i>Nil</i> or 1×40
Melt °C	195–220

6. *Type of extrusion machine.* Although the high density polythenes can be extruded successfully on single screw extruders, the twin screw machines have an advantage when working on these materials in powder form. Twin screw extruders are more easily able to work with powder feed than are the single screw machines, and can thus be expected to give a more reliable output. Apart from this, the similarity of the new materials to p.v.c. in their extrusion characteristics would also seem to indicate that multi-screw machines would be the most suitable.

An alternative system of extrusion, which is recommended by one raw material manufacturer, is to use two extrusion machines; the first to pre-heat and compact the polymer, whilst the second one carries out the extrusion, receiving a hot melt directly from the first machine. In this case the first machine could be a twin screw, and it is believed that this two-machine system is the most effective way of extruding the very high molecular weight materials.

It is also possible to prepare granules from the extrudate of the first machine so that a more normal type of extrusion process can be followed. It is doubtful, however, if this method would be as effective as the two machine system, particularly for the higher molecular weight materials. As experience with these polythenes grows, there will certainly be many changes in methods of processing, and possibly new machines will be developed to handle the high molecular weight polymer in a single pass.

THE EXTRUSION DIE

Polythene gives less apparent trouble in die design, than any extrudable material. It lends itself admirably to handling in a variety of ways, and will flow well without noticeable decomposition through dies which would be immediately condemned if proposed for other thermoplastics. Extrusion dies for polythene are, in consequence, often constructed and used in a careless manner, so that full advantage cannot be taken of these important properties.

Furthermore, although the effects of using a poorly designed and carelessly constructed die for material such as unplasticized p.v.c., for example, are immediately apparent, these effects are not so obvious when polythene is similarly misused. Judging from appearance alone, a tube or other thick polythene section which has been well extruded, does not necessarily seem any different from a similar product in which part of the material has been overheated and possibly oxidized. But, in service performance and test figures of the two apparently similar extrusions will differ considerably.

Thermal degradation of polythene in the die can occur, and its effect on the finished product—such as reduced tensile strength and lesser resistance to certain chemicals—cannot be ignored merely because the effects are not visually apparent in the extrusion.

Due care must be taken, therefore, in the design and construction of the die, to ensure smooth flow of the melt and to see that no hold up or stagnation occurs. All working surfaces of the die interior must be streamlined and highly polished. The metal from which the die is made should be such that this good surface and polish is retained for a long time, despite the screwdrivers and other unsuitable scraping instruments which will inevitably be used for cleaning. Changes of section and diameter must take place gradually, and be carefully blended to preserve the smooth flow. Steps and shoulders such as may result from badly fitting breaker plates and mandrels, etc., must be avoided and all obstructions, such as the legs of the spider or mandrel carrier, which interrupt the flow of the melt, must be carefully streamlined and given particular attention as regards surface finish.

In general terms, the function of the extrusion die is to take the circular section of the polythene melt which emerges from the barrel of the extrusion machine via the breaker plate, and to re-distribute it uniformly to the die orifice. As the material from the breaker plate is likely to be in the form of a bunch of disconnected filaments corresponding to the breaker plate holes, the die must reconsolidate this mass so that "memory" effects are reduced to a minimum.

Die orifice area in relation to machine size

For best results, the area of the die orifice must be related to the size and general design of the extrusion machine with which it is to be used. As a guiding principle, it can be taken that the maximum die orifice area

which can be economically used for polythene extrusion with dies of straight forward design, is approximately half the cross sectional area of the machine barrel bore. It can be assumed that a product of such dimensions will give little trouble on a machine with adequate output for its size, such as that described previously in this chapter. With machines of less highly developed type, which give lower outputs and, therefore, have less die filling capacity, a lower ratio should be used.

On the other hand, multi-screw machines, because of their different pressure systems, can be expected to exceed the above proportion despite their comparatively low outputs.

It is also possible by the use of dies of special construction with extra restricting devices along, or prior to the die land (to allow pressure build-up and to ensure uniform distribution of melt)—greatly to exceed this given ratio. Such devices should only be resorted to in emergency however, as a better product is usually obtainable with far less difficulty if a machine of adequate size is used.

In considering the above relationship and deciding on the correct machine for a particular job, it is important to observe that, because of draw-down and other systems of product sizing which are described later, the dimensions of the die orifice do not necessarily correspond to those of the extrusion. It is the die orifice area which is the important dimension in this, and in most other die design proportions.

Lastly on this question of die size; it should be realized that the ratio given is based on "compact" products, such as tube and thick sections generally, where no great or non-uniform pressure drop is encountered. A die for the extrusion of 72 in. flat film, for example, would require a somewhat larger machine than the $2\frac{1}{2}$ in. size suggested by the ratio!

Die length and general dimensions

The length of the complete die should be such that no convergent or divergent angle in the flow path exceeds 60° included, and preferably does not exceed 45° included. The die orifice should not be nearer to the breaker plate than a distance equal to twice the diameter of the breaker plate, and in cases where obstructions are necessary—as for tube—then a similar length/diameter proportion should be observed with regard to the diameter of the spider.

The internal diameter of the die should be such that definite compression takes place in order to consolidate the melt. To do this it is desirable, although not always possible, to effect a gradual reduction in area of the flow path, from the breaker plate to the die land, of at least 50%, and, in the case of tube dies, it is a good idea to calculate the throughput areas of the spider to ensure that this reduction can be preserved. In some instances it is necessary to design the die for a tube or other section where the area is greater than that theoretically possible on the machine being used and is, therefore, rather too large to allow the suggested 50% reduction. In these cases it is usual to consolidate

the material by causing it to flow through a narrow restricting or sizing orifice situated prior to the commencement of the die land.⁶

Die land

As will be seen in the various illustrations of dies, which accompany this chapter, the final or shaping part of the die consists of a parallel portion, land as it is called, to accept the melt from the breaker plate or the spider, and to continuously mould it to shape and dimensions suitable for final sizing. Its length must be such that memory effects and disturbances are smoothed out, and it is usual in discussions on die design, to suggest a definite ratio of land length/to die orifice thickness. Whilst an accepted ratio may be possible and can have considerable value with a material such as rigid p.v.c., its usefulness is doubtful with a relatively low viscosity melt such as polythene at extrusion temperature.

Ideally, the length of the land should be adjusted to suit the viscosity of the extrudate, but other factors will, even then, modify the final decision. The degree of restriction in the die prior to the land, the pressure in the die and the system of sizing, will all have their effect on the ideal land length and, experience based on trial and error, seems to provide the only reliable answer to this problem.

As a guide to suitable land lengths, it has been found, using melt flow index 2 on a normal die for 3 in. tube, and with a melt temperature of 145°C, that a ratio of 15 : 1 (land length/die orifice thickness) has given good results. Similarly, in the extrusion of flat film with a die temperature of 240°C, a ratio of 3 : 1 (land length/die orifice thickness) has also proved satisfactory.

The above extreme examples will also serve to illustrate the wide variations in die land lengths which are possible in polythene extrusion. Some authorities recommend the use of very long lands, such as 30 : 1, and there are cases where this is desirable, but in general the principle should be to use the shortest land compatible with good quality extrusion—beyond this point, any additional length will have little noticeable effect on extrusion quality, and will increase the die restriction and thereby reduce the output.

Die heaters and controls

The necessity for proper temperature control should be well known to all who extrude or mould polythene, or intend to do so. There is no need, therefore, to go deeply into this subject at this stage. However, there are a few important points which it is well to mention.

Die heating is usually provided by electrical resistance heaters. These may be in the form of bands to clamp on to cylindrical dies, or of another required shape. Cartridge heaters which are inserted in the body of the die are also available but should be used with care because of the danger of local overheating. Ordinary mica insulated heaters are available to give a maximum wattage dissipation of about 20 watts/sq. in.

whereas those which are ceramic insulated may be used up to a loading of double this figure. Whichever types are used, it is of great importance to make sure that good contact exists at all parts between the heaters and the die surface. In the case of band heaters, it is also good practice to provide two or more narrow bands, rather than one wide one, so that the gaps at the joins in the heaters can be staggered in relation to each other, thus avoiding a local cold area.

Except in the case of very small dies, it is best to provide two separate control points, so that the temperature at the extreme tip of the die may be somewhat higher—or in certain cases lower—than that on the main body or the back of the die. If only one control is provided on a relatively large die, the temperature is eventually a matter of compromise, and it is often extremely difficult to obtain ideal extruding conditions. The control points should also be as near as possible to the heaters they are to control. In this way accurate temperatures may be maintained whereas, if the heater is at some distance from the thermo-couples, then there will be a cyclic heat gradient between the two, and true control will be impossible.

DIES FOR THE EXTRUSION OF TUBE

Normal dies for the extrusion of polythene tube are illustrated in Fig. 17.2. Two types are given in order to show the general plan for dies of both small and large type. It will be seen that a tube die consists basically of 6 parts:

1. *The body*, which, besides locating the centring screws and the air tube correctly as regards the spider, also holds the various other parts together and forms the basis of the construction. The body should be of substantial section so that the tapped holes which retain the centring screws can give long service, and in order to provide a sufficient weight of metal to prevent localized hot spots. Under the influence of repeated expansion and contraction—to which an extrusion die is subjected during its life—and because of oxidation, screw threads always seem to give trouble. It is good practice therefore, to arrange for the die parts to be bolted together rather than for them to be attached by large diameter screw threads actually cut in the die parts themselves. A small diameter bolt which has seized up, can be drilled out and replaced by a larger one, but an outer die which has seized into a die body is a major problem, usually resulting in the destruction of one or other of the parts. The words “small diameter” in the preceding sentence must not be taken too literally however, for, although a machine designer may for aesthetic reasons prefer to use twelve small bolts, for example, the man in the shop much prefers to work with 6—or less if possible—larger ones.

2. *The torpedo or cone*, which directs the material to the webs or holes in the spider, is often machined from one piece with the spider; or it may be separate and screwed onto the spider which is provided with a

suitably screwed projecting portion. (As this part seldom requires to be removed, the precaution given above in regard to screw threads does not apply.) The latter method of construction is usually the best, and allows greater freedom for hand polishing the webs of the spider during manufacture. The final, or largest diameter of the cone must accurately mate with the centre diameter of the spider.

3. The spider, mandrel carrier, or torpedo carrier, to give it some of its many names, has as its main function the positioning of the mandrel relative to the outer die; and in the design for a small die shown in Fig. 17.2 also provides means for changing this position to achieve tube concentricity. Although in theory a concentric tube should automatically

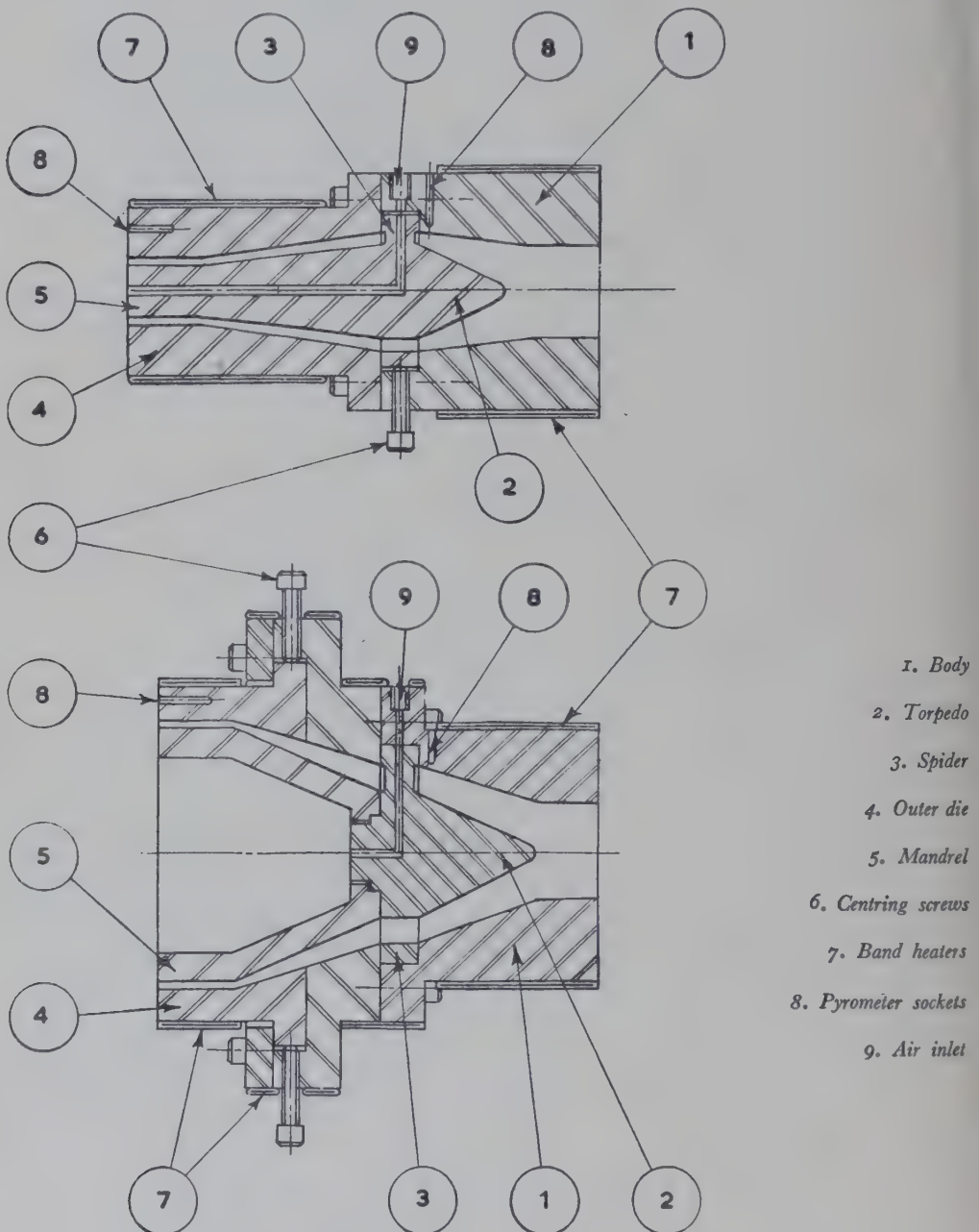


Fig. 17.2. Type of extrusion dies suitable for large and small tubes

result if the mandrel is truly located centrally within the outer die, it is found in practice—due to unpredictable flow disturbances etc.—that this is seldom true, and some provision for adjustment is essential.

The form of die construction referred to above, i.e. with an adjustable mandrel, applies to relatively short dies for tube up to about 3 in., in which range it is very suitable and convenient. For larger dies as also shown in Fig. 17.2, the unsupported length of the mandrel renders adjustment by this means erratic and unreliable. In such dies, therefore, it is better for the mandrel to be fixed, and for concentricity to be obtained by movement of the forward part of the outer die as shown.

The spider must be substantially constructed, so that the mandrel is firmly held in position against the pressure—sometimes considerable—of the polythene melt. The thickness and number of the webs therefore, is a compromise between strength and degree of interruption of flow. Each web is given a streamlined shape, and may be from $\frac{3}{8}$ in. to $\frac{1}{2}$ in. at its thickest part. The number of webs varies from 3 to 8, or more, depending on the die size, and one or all of them are drilled radially to the spider centre to give passage for inflating air. The outer ring of the spider must also be strong enough to resist the heavy thrust of the centring screws without distortion, and its inner diameter must mate accurately with the bores of the outer die and die body.

In order to allow lateral movement of the spider without loosening the outer die retaining screws—which is very bad practice—the fore and aft dimensions of the spider ring, together with the depth of the recess in which it fits, must be accurately controlled to give an interference fit when all retaining bolts are fully tightened. This applies equally to the adjustment flange on the forward part of the outer die in dies constructed with a fixed mandrel.

Although the form of spider construction shown uses a small number of radial webs of streamlined section as a means of supporting the mandrel, it is also possible to achieve, roughly, the same purpose by drilling one or more rings of accurately spaced holes. This method of spider construction obviously entails much less labour and, as a result, is frequently used. Unfortunately, however, it is very difficult to obtain good streamlining with such a design and the honeycomb-like obstruction to the polythene has a greater tendency to introduce disturbances to the flow. If this design is adopted therefore, it is always necessary to allow ample distance between the perforated spider and the commencement of the die land. Another difficulty with this method of construction is that there are no conveniently placed radial webs in which to drill the hole for inflating air. The usual method of overcoming this, is to arrange a tightly fitting tube of small dimensions to pass radially through the honeycomb.

4 and 5. *The outer die and mandrel.* These two parts together constitute the actual tube-forming annulus of the die. Both members must form accurate stepless joints with their respective mating portions of the

spider. The mandrel is drilled longitudinally for inflating air, to connect up with the previously mentioned hole drilled radially in one of the spider. Both the outer die and mandrel are coned to converge or diverge into the die land, and are of suitable length to conform to proportions previously given. The convergent or divergent angles are arranged to give the required compression in the most convenient manner. One of the problems associated with the design of tube dies, arises from the fact that the thermoplastic material destined to form the exterior of the tube, must travel a greater distance than the material which will eventually be on the inside. Furthermore, the frictional area of metal to thermoplastic is also greater on the outside. It is true that the outside material is nearer to the source of die heat and will, therefore, be of lower viscosity but, despite this there is always a tendency for the material at the outside to travel at a lower speed than that on the interior.

This is one of the reasons for the sometimes different appearance of the bore and outside diameters and, in some cases, is also responsible for the wavy or rippled bore seen in many tubes.

It is not possible to equalize the metal/plastics inside and outside frictional areas, but it is possible, by careful design, to minimize the effect.

It is desirable, therefore, to avoid the use of angles which differ widely on the outer die and mandrel coned portions; and rather to obtain the required reduction in cross sectional areas by change of diameter, so that the material on the inside must describe a path which is similar to that on the outside. This will usually entail the use of a spider whose minimum flow path diameter or central core is somewhat greater than that of the mandrel land.

These conditions do not apply to the same extent to tube dies with divergent angles, i.e. for large tubes of 6 in. and over, as the difference here are not so apparent.

6. *The centring screws.* If the die has been designed, constructed and used according to the recommendations which have been outlined, it will be reasonably certain to give a good extrusion. Its ability to produce a good saleable, concentric tube, however, is dependent on the centring screws whose function is to move one part of the die relative to the other, against the considerable working pressure, whilst the extrusion machine is in operation.

These screws, therefore, are an extremely important part of the die. Yet, in the writer's experience, it is common for them to be considered in a relatively casual way, as a few screws which are put in as somewhat of an afterthought. In consequence therefore, failure of centring screws is—also in the writer's experience—one of the most common causes of production stoppage, and in order to minimize this risk of failure, the following recommendations are given:

(a) Centring screws should always be of substantial size: $\frac{1}{2}$ in. diameter being the minimum, even for quite small dies; and $\frac{5}{8}$ in. or even $\frac{3}{4}$ in. sizes should be used wherever possible.

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(b) The screw thread should be fine—B.S.F. is recommended—so that small adjustments can easily be made. They must, however, be easily procurable standard items, to provide for ready replacement.

(c) The screws should be of high tensile steel, and the first two threads adjacent to the spider or other part, should be machined away so that, in the event of mushrooming, the screw may still be extracted.

(d) Perhaps surprisingly, four screws are found in practice, to give the best and easiest centring adjustment. In the case of large dies, eight screws should be used.

(e) Centring screws and sliding faces should always be smeared with silicone grease during assembly of the die.

Design for cross head

The dies for the extrusion of polythene so far described, are designed for the normal straight through attachment to the extruder. It is equally

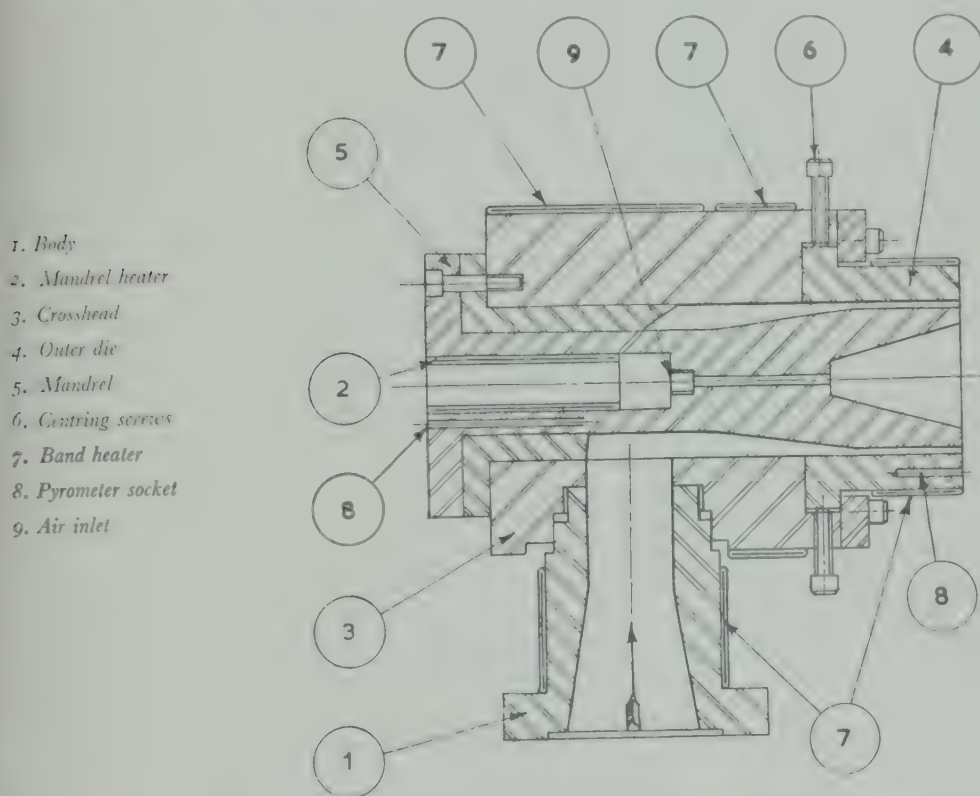


Fig. 17.3. Cross head die for polythene tube extrusion

possible to use the cross head method, Fig. 17.3, and here, the same principles of design apply.

The cross head has some advantages over the more normal system, in that it allows greater freedom of design for a wide range of sizes. It also allows of a more rigid construction as regards the mandrel and its method of attachment to the die body, and avoids all difficulties with regard to the use of inflating air.

The cross head also gives access to the back of the mandrel and thus makes the temperature control of this member a relatively simple matter.

And, as there is no spider or other flow interrupting part, lines and disturbances from such a source cannot occur.

On the other hand, there is always the difficulty of obtaining uniform flow with a cross head, and troubles with this tend to increase as diameter goes up. Most people, therefore, prefer the small, and

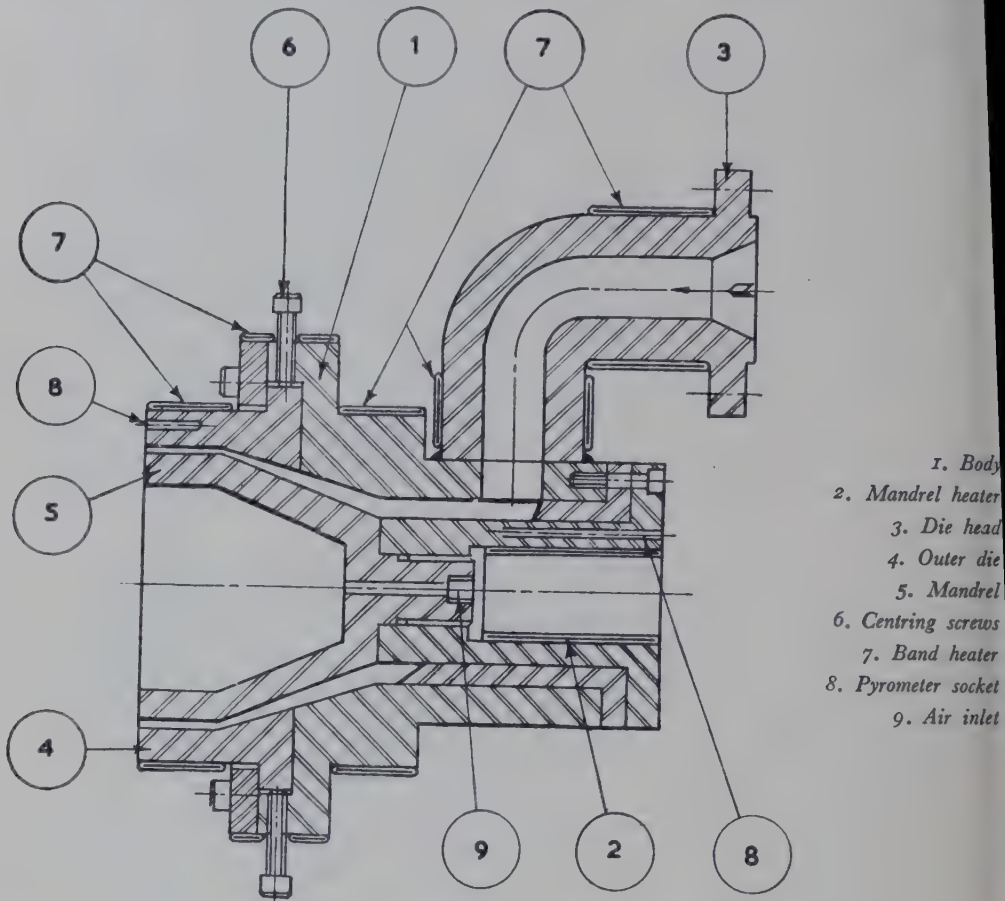


Fig. 17.4. Offset die for polythene tube extrusion

understood, inconveniences of the straight through head for tube production, although the cross head method is now normal in the manufacture of polythene tubular film and flat film.

A further interesting system of die attachment, which has been developed from the cross head, is the offset die. This is, in effect, a "double cross head", in which the material is made to change direction twice; the advantage being that the extrusion is still in line with the extruder (Fig. 17.4.)

DIES FOR THE EXTRUSION OF SOLID SECTIONS

Dies for the production of solid sections, although conforming to the same rules, are basically much simpler than those for tubes, as there are none of the many problems associated with mandrels and spiders, and inflating air, etc. Profile dies normally consist of nothing more than a basic coned portion—called the retainer block—which is attached to the extruder; and an interchangeable die plate in which the required die

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profile is cut and blended out to suit (Fig. 17.5) the mating bore of the coned portion. The die plate may be multi-piece to facilitate manufacture. Dies for the extrusion of rod, are nothing more than tube dies from which the mandrels, spiders, etc., have been omitted, and to which extra long lands have been given. (Fig. 17.6.)

No specific rule can be given for the design of profile dies, as every new shape presents its own new problems. Frictional drag on the material in its passage through the die, must be compensated for, as must the

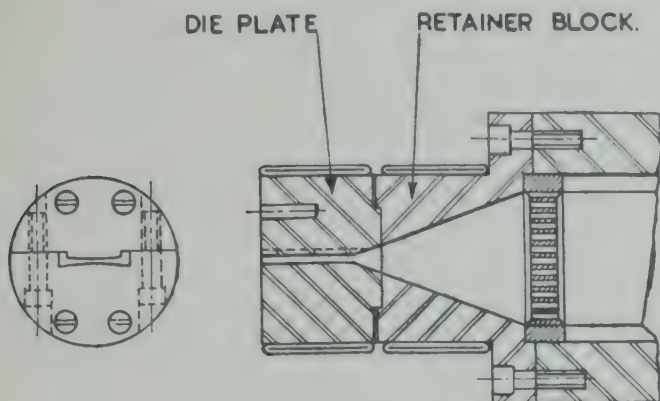


Fig. 17.5. Extrusion die for wide channel section

tendency for material flow in thick parts to be disproportionately large compared with that in thinner parts. The shape of the die orifice, therefore, is seldom similar to that of the extrusion from it.

Taking as an example a $\frac{3}{8}$ in. square rod—a very difficult die design by the way—the above points may be well illustrated. If the die is constructed as a true square, material flow will be greatly restricted in the corners, and very free in the centre. The resulting extruded profile will, therefore, be shaped as shown in Fig. 17.7. In order to compensate for this, the die must be profiled somewhat on the lines shown. It will be noted that a true radius from corner to corner will not achieve the required

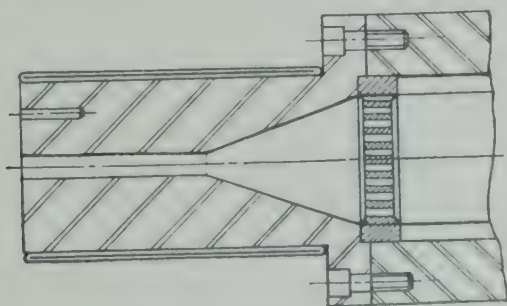


Fig. 17.6. Normal extrusion die for polythene rod

result, as this increases the restriction at the corners. Correction may also be applied by local adjustments to land length and it is normal practice to use a combination of the two methods.

It can be seen that a complicated profile consisting of a number of different thicknesses, and various corners or angles, can present con-

siderable difficulty as regards shape. It is usual therefore, to produce the die in an unfinished form and to arrive at the correct profile by trial and error on the actual extrusion machine with which it is to be used. The writer has seen a die of this type which required 20 hand adjustments before the correct profile was obtained; even then it could not be used on the machine used for the trials, and under identical conditions

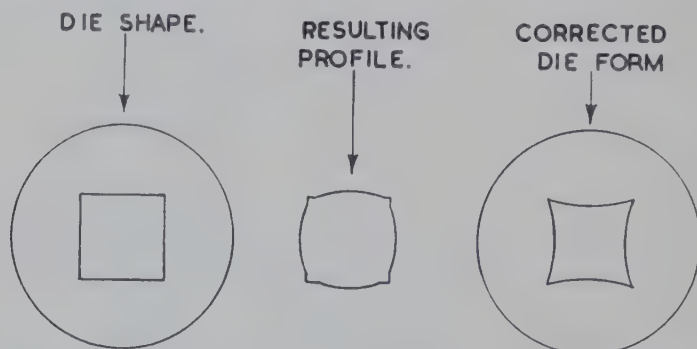


Fig. 17.7. Illustration, showing differential flow in profile dies

Overall size control of an extruded profile in polythene is usually obtained by adjustments to the speed of take-off, by the methods to be described later. Also, the production of good extrusions free from waviness, etc., is largely dependent on the use of tension to draw the product into the cooling medium. The die profile therefore, must be somewhat larger than that of the required section. It is usual to allow a 25% to 30% increase, although in some cases as much as 100% is used.

This question of draw-down also brings its own problems, which must be borne in mind, in regard to the actual shape of the die profile. Thick sections, such as $1\frac{1}{2}$ in. \times $\frac{1}{8}$ in. strip, or the square previously mentioned, will draw down more or less uniformly, although the corners may change a little. Thin sections, however, tend to draw more in thickness than in width, an excellent though exaggerated example of this being polythene flat film which uses a die with 0.025 in. gap to give a 0.001 in. film with the loss in width of only about 10%.

Little can be said about rod dies as the problem here is rather one of cooling, which will be dealt with in a later section. The dies themselves are obviously very simple, as there are no problems of profile. The land length must be great enough to allow the build-up of adequate pressure in the screw and die, and this often calls for a very long die, usually of special form. For reasons which will be given later, it is often considered uneconomic to attempt the continuous extrusion of polythene rods in diameters greater than about $\frac{3}{4}$ in. Most firms prefer to extrude into a closed mould for such work.

EXTRUSION DIES FOR HIGH DENSITY POLYTHENE

Although extrusion dies for the high density materials can be constructed in the same manner and by observing the same rules, as those for the low density polythenes, there are one or two points which must

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receive special attention. Because of their higher melt viscosity, the new materials will not flow so readily, so that particular care must be taken with the streamlining of the flow passages, and with changes of form and section.

Again, possibly because of the relatively high viscosity of some materials in the die, more difficulty is experienced in consolidating the extrusion into an unbroken annular mass after it has passed through the breaker plate or through the spider of a tube die. In order to be certain of complete rewelding at these points therefore, particular care must be taken to see that the distances from breaker plate to die land, or from spider to die land conform to the rule given earlier on this point. An extra long die land—i.e. of the order of 30 : 1 is also useful in this respect.

With some of the high density materials, as at present available, the catalysts used in the polymerization process seem not to have been completely removed. These catalysts, although they can only be present in the polythene in a minute proportion, seem to cause corrosion of the extrusion dies and calibrating devices, etc., after a period of running. The effect of this corrosion is to form deposits on the die lands, etc., which mark the extrusion. All dies and forming devices, therefore, should be either of some corrosion-resistant steel, or chromium plated.

From the above cautionary points, the similarity of the extrusion behaviour of high density polythenes to that of unplasticized p.v.c. will again be observed.

The remainder of the extrusion process which is described in detail in the following pages requires no change or modification for high density polythenes. The descriptive matter and data can, therefore, be taken as equally true for both types of material.

EXTRUSION SIZING AND FORMING DEVICES

In the early days of polythene extrusion attempts were made to produce extrusions directly from the die. Unfortunately, however, the fluidity of polythene at its extruding temperature, caused the products to distort or collapse under their own weight, and it soon became obvious that some method of holding the extrusion to the required shape and size, whilst at the same time rapidly chilling it, was essential.

Considerable experimental work in connection with these problems has been carried out therefore, and has resulted in a number of ingenious devices for precise dimensional control. Because of the very wide range of extruded products called for in the extrusion industry, it is obviously difficult to devise a single universal system so that the method used must be selected according to the job.

In order to discuss the important methods, therefore, it is convenient to separate them into classes under product headings.

Sizing devices for tube

It is now possible to purchase from a number of machine manufacturers, the complete equipment adaptable to any size of tube within the capacity

of the extruder. The most common method, which was first of the writer's knowledge in 1946, uses a water cooled former or sizing die the bore of which is machined to the outside diameter of the extruded tube, plus a calculated allowance for shrinkage. In this method the extruded tube which comes from the extrusion die, is continuously inflated to the size of the sizing die bore, the end of the tube being sealed—so that its outside diameter is in contact with the chilled surface of the sizing die bore and the tube is thus frozen to form and dimensions.

The sizing die, one form of which is shown in Fig. 17.8, consists of a water jacketed tube, the bore of which is given a sand-blasted finish to minimize adhesion, and which is attached to, but heat insulated from, the extrusion die. The length of the sizing die must be such that the polythene tube is substantially frozen during the contact period, and is dependent therefore, on the wall thickness of the tube and its linear speed and the type and effectiveness of subsequent cooling. The extrusion die bore should be about 20% smaller than the bore of the sizing die for tubes up to and including $1\frac{1}{2}$ in. o.d., and 10% smaller in the case of sizes above this. The diameter of the extrusion die mandrel is critical, as the wall thickness of the finished tube is controlled by

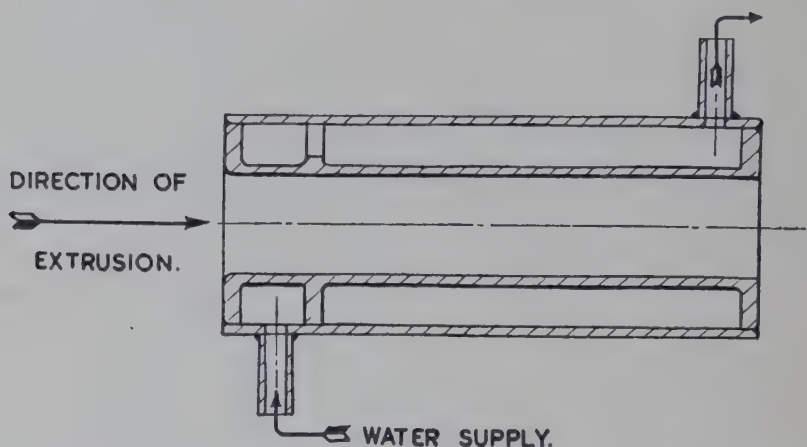


Fig. 17.8. Normal water-cooled former for polythene tubes

speed of take off. It is usual however, to provide a die annulus whose width is such that a cross sectional area about 10% greater than that of the finished tube is given.

It must be emphasized that the chilled former method of sizing, one variation of which has been briefly described, can be used in many ways. In some cases, the former is in actual metallic contact with the extrusion die; and in others it is separated from it by varying distances up to 3 inches or more. A further system uses only a very short former attached to the extrusion die, and passes the tube into a second and longer sizing die, allowing a gap between the two the length of which is dependent on the internal air pressure. An even further variation uses vacuum to hold the tube to form, rather than applied internal air pressure, and thus avoids

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the necessity for sealing of the tube: and others dispense with the cooled former and use extended cooled mandrels.⁷ Some of these variations have formed the subject of previous work⁸ and of patents.⁹

The method of tube size control using a chilled former or sizing die, is particularly suitable for tubes of medium and large size. Its use however, in the manufacture of small diameter tubes, i.e. of outside diameter less than about $\frac{3}{4}$ in., is attended by considerable practical difficulty which increases as the size is reduced. In the case of a tube of $\frac{1}{2}$ in. o.d. with a wall $\frac{3}{32}$ in. thick for example, it is easily seen, allowing for a reduction of 20% in the outer die i.d. and providing the 10% excess in cross section area, that the mandrel diameter becomes excessively small. Under such conditions there would be a great tendency for the former to fill up and become solid with material, and a large number of attempts would probably be necessary before the job could be made to run.

Another system of sizing is used therefore for small polythene tubes, and is shown in complete form in Fig. 17.11.

This method uses an extrusion die which is considerably larger than the required final size of tube, and draws the product through a sizing plate which forms one end of a water bath. As in the previous system, the tube is prevented from collapse by internal air pressure, and the end is therefore sealed. The method depends for its success on rapid draw-off, thus relying on the tension given to the product, to prevent sag and consequent distortion.

The sizing plate is bored to the required final outside diameter of the tube, and it may be backed up by one or more further plates situated in the water at a distance of approximately 3 in. to 6 in. from the first one. The far end of the water bath is constructed to accommodate a gland to prevent loss of cooling water. The wall thickness of the product is controlled by speed of take-off, and the outside diameter by the sizing plate: sufficient air pressure being given, so that the tube just fills this plate without any pronounced bulge between it and between the extrusion die.

As with the water cooled former method, the above system is also capable of wide variation, and various extensions of it have been the subject of patents.^{10, 11}

One such variation uses a tubular die in place of the die plate, whilst another uses a curved tube so that the product may be taken into the water bath vertically, or at an angle; thus dispensing with the die plate. It is also possible, with a very small tube, to dispense with the sealed end and allow the inflating air to escape to atmosphere. This has the disadvantage that there is a gradual increase in pressure build up and therefore diameter, as the uncut produced length increases. A better method for such small tubes is to use atmospheric air only, carefully adjusting the die size so that inflation control is no longer essential.

Whenever a system of tube sizing involving internal air pressure is used, there are two matters which usually present problems.

Firstly there is the question of sealing the tubes to preserve air pressure. When a small diameter product is being manufactured this does not present a great problem, as the tube can easily be pinched by hand at the die prior to cutting off the complete coil, and if the dimensions are greater, making the hand method difficult, then a screw operated clamp can be used on the cold tube prior to cutting.

When the tube is of large diameter, such that it is not coilable, the problem can be considerable. Various ingenious devices have been developed to overcome this, and the most usual one uses screw operated clamps which remain with the tube as it passes away from the die; another clamp being attached before the tube length is cut off.

Such systems are not elegant however, and are very wasteful of material, particularly with large diameters. Much attention has therefore been given to developing methods of sealing which allow the tube length to be cut off without disturbing the inflating pressure. A certain amount of success has come from this work, and some of the results form the subject of patents.^{7, 12, 13}

The second inflating problem concerns the provision of an accurate and controllable supply of constant low pressure air, and it cannot yet be said that the complete answer to this is available. The air pressure commonly used in tube manufacture is of the order of 1 lb/sq. in., and in the second method of tube sizing described—where a chilled former is not used—the diameter of the tube will follow even the minutest fluctuation in this pressure. To keep within commercial tolerances the variation of the supply must not exceed 5%. And 5% of 1 lb/sq. in. is a very small pressure indeed, to which most control devices will not respond.

One of the most successful methods adopted so far, is to use a separate rotary blower as part of the die equipment. The air from the blower passes into a reservoir and from there to the die via an adjustable bleed, a cone valve and a U tube manometer.

Form preserving devices for profiles

Very little specific information can be given on the sizing of polythene profiles, because, as with profile die design, each different shape presents its own particular problems. However, in general it can be said that the system most usually adopted, resembles that used for the sizing of small diameter polythene tubes.

The profile is extruded from a die which is considerably larger than the orifice area than that of the required section, and is drawn down through a shaping—or shape preserving—plate or plates into a water bath. The profiles cut in the shaping plates are not complete female reproductions of the required section, but are rather rudimentary, in that their purpose is mainly to prevent collapse rather than to do any actual shaping. The extrusion contacts the plate profile, therefore, only at small points as are likely to collapse or distort, and the remainder of the shaping orifice is lined with soft felt or some similar material, and acts merely as a water gland.

EXTRUSION OF TUBE, ROD AND PROFILE

Shape and size control are given by the construction of a correct die, as previously described, and by the speed of take-off.

As the polythene extrusion is very soft and delicate when it leaves the extrusion die, great care is required in handling it, and even very light contact with the felt in the shape preserving device may be sufficient to cause serious distortion. It is usual therefore, to give the profile a preliminary cooling, immediately it leaves the extrusion die so that the outside skin is sufficiently set up to resist such effects whilst still retaining the molten interior to undergo shape corrections if necessary. This is done by passing the profile through a tube through which a controllable current of cold air is passed. The direction of this current must be so arranged that it acts equally around the soft profile and does not itself cause distortion.

Although a general method for handling profiles has been given, it will be appreciated that there are many other methods in current use. Sometimes the section is extruded vertically upwards, and at others it is extruded downwards into a water bath. Another method relies on the extrusion of a section which will collapse, under control, into the required form. The method to be adopted can only be determined by a careful study of the individual profile.

Sizing methods for polythene rod

The extrusion of polythene rod is a rather special case, in that the extrusion die is approximately the same size as the required product. It is also unique in that there are few problems of collapse and distortion to be overcome. There are, however, other problems which have often been found so difficult to overcome that many users of polythene rod prefer to produce it by the discontinuous and slow method of extruding into a closed mould. As such rod has so far been a relatively unimportant product, as far as tonnage is concerned, this method has proved quite suitable.

The first problem is associated with the flow pattern of a thick section in an extrusion die. Because of the distribution of pressures in such a die, and also because of the frictional effects of the walls of the die, there is a pronounced tendency for the material to extrude at a higher speed in the centre than at the outside. This gives an unreliable product, which is internally stressed, and which may develop cracks in service. The trouble may be overcome by using a long lubricated die which is water cooled for the last part of its length, so that the rod is cold throughout by the time it reaches the open air.¹⁴ It is usual to apply braking forces by friction bands, or other means, to the cold part of the rod as it passes through the long die, thus making sure that the molten extrudate nearer to the extruder is working against pressures which are equal over its entire area. Other systems of doing this have been developed and are the subject of patents.^{15, 16, 17}

The other problem encountered in the extrusion of rod, and also to some extent in the extrusion moulding of the product, is the production

of voids due to differential contraction. When the extrudate leaves the rod die, it is substantially uniform in temperature, and is homogeneous. Immediately any cooling effects act on it however, the tendency is for the exterior to cool first whilst the interior remains molten for a considerable period, depending on the thickness of the product. The coefficient of expansion of polythene is high, and in cooling from molten to ambient temperature, a substantial section will show a considerable reduction in volume. There is also an additional and even more important reduction in volume due to the change which takes place at the transition temperature.

In the partially cooled product, referred to above, the outside is set up to a fixed size whilst the interior has still to undergo contraction as it cools, and the formation of voids will be inevitable.

A number of methods have been discussed in attempts to overcome this trouble, and in general there are three systems of approach. The first system is to cool under pressure: such as with the special long die described above; and by other similar methods. The second is to give extremely rapid and efficient shock cooling immediately the product leaves the die, in an attempt to cool throughout: and the third, in common use in the cable industry,* is to cool very slowly so that the outside does not set up more quickly than the interior.

Of these methods, the third one is the most frequently used, as it is reasonably efficient and relatively simple to apply. The product is passed through two, or more, separate water baths, arranged end to end which are at different controlled temperatures. The first one being almost at boiling point, and the last one at ambient temperature. In this way, the outside of the product is prevented from chilling before the interior, and the rod can, therefore, be expected to be free from voids.

The second method, i.e., the rapid shock cooling, is usually effective only on quite small diameters.

Although the above methods are used with considerable success, it is well to point out again that the continuous extrusion of reliable, void-free polythene rod, of diameters greater than about $\frac{3}{4}$ in., is an extremely difficult operation requiring much experience and practice.

COOLING SYSTEMS

In a previous section of this chapter, methods were discussed for chilling a tube or other polythene product to the required size and form. Although in very thin sections this chilling may well be all that is required, it is emphasized that, with the average product, such as tubes with $\frac{1}{8}$ in.— $\frac{3}{16}$ in. wall thickness, and profiles of similar dimensions, considerable further cooling is required if subsequent deformation is to be avoided.

Products which are sized by drawing into a water bath via a sizing plate, etc., automatically obtain this extra cooling by their passage

* See Chapter 16.

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through the water bath, although it is essential that this equipment be of adequate length. It remains necessary, therefore, to describe only the systems of additional cooling for tubes which have been sized by means of a water cooled former.

Water cooled formers or sizing dies, normally vary in length from about 4 in. to 12 in., depending on the tube size, its wall thickness, the linear speed of the product and the practical difficulties attendant upon threading a tube of molten material through a long, small bore tube.

Whatever practical length of former is used within the above range, it will be obvious that the mere passage through the former of the tube from the extrusion die, even though the two are in good contact, will only cool a thin layer on the outside of the polythene tube. Although this is sufficient to size the product temporarily, the still molten interior will quickly communicate some of its heat to the chilled skin and cause subsequent collapse if additional cooling is not immediately applied.

The first method to be adopted for the supply of extra cooling, was by means of air jets. This, however, proved to be inadequate and was substituted by water sprays. The method now universally adopted, is to pass the tube from the water cooled former directly into a water bath via a rubber gland. Some systems substitute a second forming tube for the rubber gland, in an attempt to obtain additional size control. A similar rubber gland is situated at the far end of the water bath and others are provided at regular intervals along its length, to act as tube supports. The minimum length of water bath suitable for the production of a range of polythene tube, is 8 ft.; a shorter bath than this does not usually give adequate cooling and baths of 20-30 ft. are often used.

TAKE-OFF SYSTEMS

The take-off system is the means whereby the tube, profile or other polythene product such as cable* is drawn away from the extrusion die under controlled tension, through the sizing and cooling devices and is passed to the coiling drum or other finished product handling equipment.

In considering the question of take-off for any particular product, it is important to realize that the extrusion systems outlined in the previous pages, depend for their successful operation on smooth and uninterrupted movement of the product at an accurately controlled speed.

If the action of the take-off is erratic, or jerky, or if it does not grip the product in a sufficiently positive manner, then the extrusion will be equally erratic in dimensions, which will accurately portray each jerk as an increase or decrease in cross section. In extreme cases, if the jerk is violent amounting to almost a temporary stoppage; or if the slip is particularly bad, then it is possible for the extrusion to freeze in the sizing device causing complete breakdown of the process.

If, on the other hand, the take-off grips too well it may cause permanent distortion of the product. The grip, however, must not only give positive

* See Chapter 16.

draw to the product under all conditions, but it must also be sufficient to allow the coiling or other movements of the finished extrusion to take place after the take-off, to be carried out without risk of distorting the extrusion at the die or in the sizing and cooling devices. The sensitivity of the grip must, therefore, be accurately and easily controlled whilst working, so that the most suitable compromise can be found.

All extrusion systems for polythene, irrespective of the type of product, depend for size control on a precise adjustment of the linear speed of the take-off in relation to the actual speed of extrusion. The variable speed drive therefore, with which the take-off is fitted, is one of the most important pieces of equipment in the whole system. Speed variation must be over as wide a range as possible, and its adjustment should be smooth and fine, so that precise small speed differences can be obtained with certainty. Some form of positive indication of the actual speed of the extrusion is also necessary, so that the extent of such changes can be followed, and so that the original speed can be restored if necessary.

The actual form of the take-off equipment is dependent to a large extent on the type of product it is to handle. In practice there are a number of basic types in general use; each of which is more suited to a particular class of extrusion, but which must each be capable of considerable modification for individual products within their classes of application.

It is generally accepted that certain products, such as flat strips; very shallow channel-like sections with a flat base; small diameter tubes, i.e. up to about $\frac{3}{8}$ in. o.d., are more suitably taken-off on a conveyor band, whilst extrusions requiring a greater tractive effort such as medium and large sized tubes and rod etc., are better handled on nip rollers. It is also found that complicated sections with no particular base line can be more easily held to form without twists etc., on nip rollers.

A good type of general purpose conveyor band for polythene extrusion will be at least 12 ft. in length and 4-6 in. wide. Provision must be made for cooling the band, if possible by means of a water trough through which it passes on its return run. In order that the product will be gripped positively, which is sometimes difficult with light products of small section, at least one adjustable weighted pressure roller must be provided at the far end of the band. These rollers must be readily interchangeable, and profiled to suit the particular product.

The belt itself will be of canvas-reinforced neoprene—or some similar material—and must have no detectable pattern on its upper surface to mark the extrusion.

A nip roller assembly consists of a number of pairs of rollers—i.e. at least four—which are profiled in such a way that they give the maximum grip on the product without producing permanent deformation. The lower rollers are all driven from a common shaft, so that they run at identical speed; and the upper ones are usually free running and adjustable with adjustable pressure, so that the degree of deformation

EXTRUSION OF TUBE, ROD AND PROFILE

the product can be controlled. If the nip roller assembly is to be used only for tube, then the rolls can be of adjustable width Vee type, which will give four points of contact on the tube. If, on the other hand the equipment is to be used for a variety of products, including profiles,

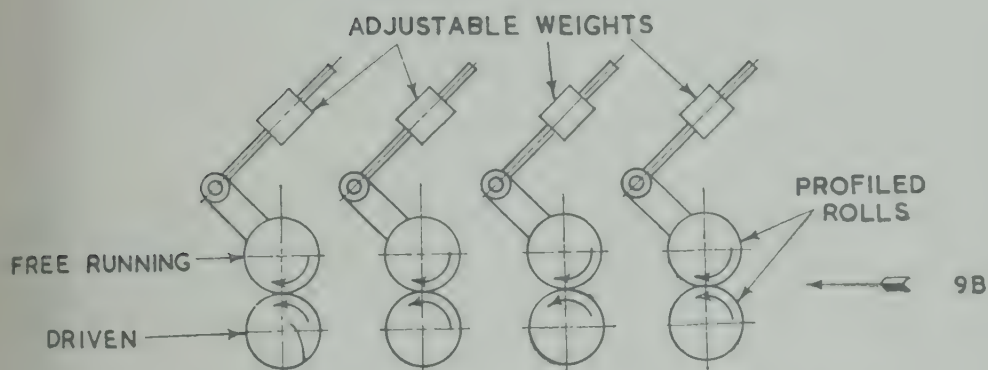
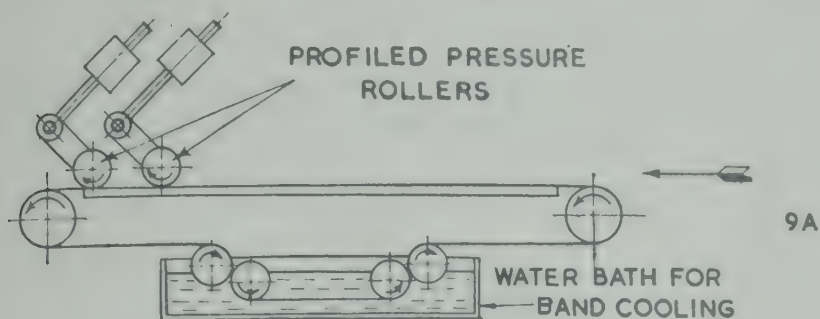


Fig. 17.9A and 9B. Diagrammatic illustration of conveyor band and nip roller take-off for polythene extrusion

then the rolls must be easily interchangeable so that others, specially profiled for the individual product can be placed in position.

Diagrammatic illustrations of both types of take-off are shown in Figs. 17.9A and 17.9B, and it will be useful at this stage to summarize the necessary features which must be provided by both systems:

1. The take-off must grip the extrusion positively at all times, irrespective of the considerable changes in dimensions which sometimes occur.
2. The pressure on the product due to the action of the weighted or pressurized upper rollers, must be adjustable from nothing up to a maximum, depending on the maximum tractive effort required.
3. In order to provide for starting, and for emergencies, etc., the pressure rollers must be capable of being quickly lifted out of the way.
4. The take-off must be driven by a good system of variable speed drive with remote control, so that the speed can be adjusted from the extruder.
5. The drive must be absolutely smooth throughout its entire range, and some accurate indication of linear speed must be provided at the extruder, to be used in conjunction with the remote control.

6. The rolls must be interchangeable, or otherwise adjustable to requirements of the product being handled.
7. In order to avoid introducing curvature to straight lengths there the height of the take-off should be finely adjustable.

EXAMPLES OF COMPLETE EXTRUSION SYSTEMS

Having now described in some detail the various individual components which are necessary for good polythene extrusion, it is possible to describe the various complete systems which consist of assemblies of selected

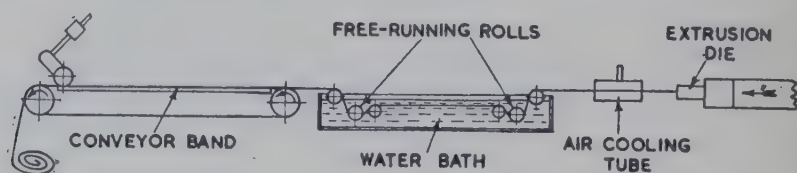


Fig. 17.10. Schematic arrangement of extrusion system for flat strip

To do this, it will be convenient to describe the production system for one or two typical products.

(1) $2 \text{ in.} \times \frac{1}{16} \text{ in.}$ flat strip

Fig. 17.10 shows, diagrammatically, a suitable process for the manufacture of the above product. The extrusion machine of suitable type, is equipped with a breaker plate and gauze screen filter pack. The extrusion is 50% greater in thickness, and approximately 25% greater in width, with the corners carefully filed out or the lands locally reduced, to ensure equal flow at these points. The extrusion is taken through a cooling tube into a water bath via a pyramid of free running rollers, to prevent wrinkling, and is taken out of the water by further rolls at the far end. The take-off consists of a conveyor band equipped with a weight pressure roll, and once accurate die proportions have been established

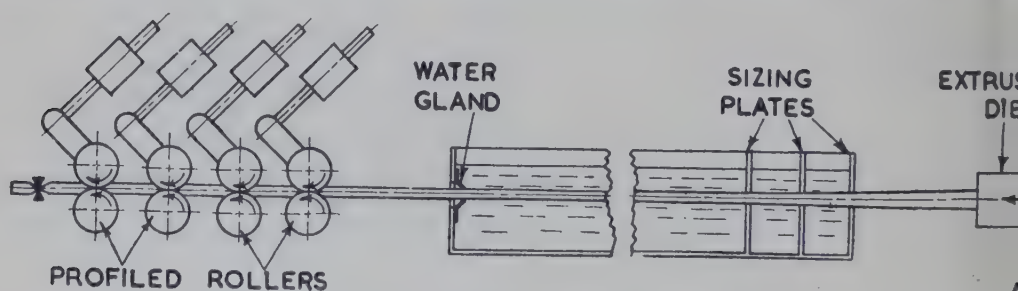


Fig. 17.11. Schematic arrangement of extrusion system for small polythene tubes

dimensional control is given entirely by careful adjustment to conveyor speeds. The product is cut into the required length on some form of automatic cutter, or is coiled on a winding device which may be electrically driven—or in some other manner to give control of tension from the take-off.

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(2) $\frac{1}{2}$ in. diameter tube

The system for the production of this product is shown in Fig. 17.11 and consists again, of the extruder, screen pack, etc., which this time, is equipped with an extrusion die 50% oversize. The tube is drawn by means of a series of nip rollers, through a number of sizing plates, and into a water bath. The far end of this bath is provided with a simple gland consisting of a rubber washer, to prevent loss of cooling water. It may also be necessary to provide a degree of cooling between the die and the first sizing plate.

(3) 2 in. diameter tube

In this example (Fig. 17.12), the extruder is equipped with a water cooled former and the product is drawn, again by nip rollers, through a water bath which is provided with rubber glands at each end. Other glands of similar type may be placed at approximately 18 in. intervals along the length of the water bath to preserve straightness in the product whilst it is undergoing cooling.

FORMS OF DESPATCH

Finally, it will be useful to consider briefly the question of the method of presentation of the finished product for sale. In this, of course, very much will be determined by the eventual end use of the extrusion. Profiles are usually requested in accurately cut lengths, so that they may be used without further operations, and with complicated sections where

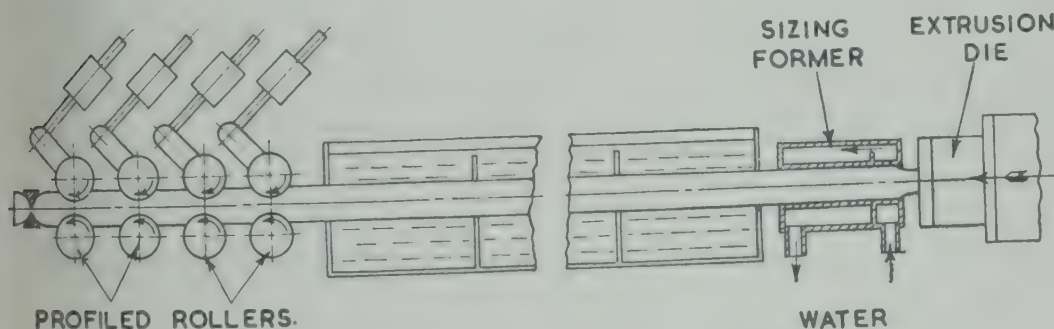


Fig. 17.12. Extrusion system for medium and large diameter polythene tubes

there is a considerable risk of distortion, such as curvature, etc., this method of supply is the only feasible one. Small and very small tubes, are supplied coiled, either on cardboard drums or self supporting, depending on the dimensions of the tube. Large tubes, which are too rigid to coil, are supplied in random lengths. Tubes of medium size, i.e., 1-2 in. bores inclusive, may be supplied either in straight lengths, or coiled according to the requirements of the eventual end use. If such sizes are supplied in coiled form, it is important to give attention to the size of the coil in order to minimize the risk of permanent curvature, and suitable minimum coil diameters have been specified in B.S.1972 and B.S.1973. As a further precaution against permanent curvature, or

other forms of distortion, it is advisable to make sure that poly products are cooled throughout, to below 30°C before coiling or into bundles for despatch.

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THE EXTRUSION OF TUBULAR AND
FLAT POLYTHENE FILM

E. G. FISHER

IN general, it can be said that the manufacture of polythene film is a more critical process, requiring more attention to detail than extrusion processes for the production of thicker sections in this material. With a thick walled tube or other similar product, a considerable lack of homogeneity could be obscured within the thickness of the extrusion with little apparent ill effect on the product. Similarly, the small longitudinal marks which sometimes occur as a result of memory effects, and due to disturbances of the flow pattern within the die, do not show on a thick section. Further, the presence of one or two small die lines, due to a foreign body on the die land for example, does not often materially reduce the strength or usefulness of a thick polythene product.

Any one of these defects, and a number of others of a similar order would be sufficient to cause the rejection of a film product.

Due to the thinness and transparency of polythene film, any lack of homogeneity, besides being immediately apparent and unsightly, will give a film of reduced strength which may also be porous. A line, due to partial obstruction of the die land for example, which might only penetrate to 0.5% of the depth of a thick section, could easily reduce a film thickness by 50% to cause a very weak band or local area.

Another factor which emphasizes the critical nature of film extrusion processes, is the need for very close thickness tolerances. A local longitudinal increase in thickness of a few thousandths part of an inch will have very little effect on the value of a polythene water pipe, for example. But a longitudinal thick band of only 0.0005 in. will cause a substantial swelling in a roll of film as successive layers build up, and will result in cold stretching and deformation of the outer layers at this point.

These few examples, which could have been much enlarged upon, will serve to underline the need for great care at each stage in the extrusion of polythene film.

Following upon this, it will now be convenient to give a brief resumé—from an extrusion point of view only—of the properties required in a good polythene film, whilst the remainder of this chapter will attempt to describe in detail how these requirements can be satisfied.

1. The product must be as free as possible from the blemishes, and spots of non-homogeneous polythene commonly called "fish-eyes". It must also be free from pinholes.

POLYTHENE

2. The film must be free from extrusion lines and local longitudinal thin or thick bands.
3. Unless required for a special purpose, the lateral strength of the film should not differ greatly from that in a longitudinal direction. This applies more particularly to tubular film.
4. The film must be bright, and as clear as possible without having undue "blocking" tendencies.
5. The thickness of the film must be uniform throughout, both longitudinally and laterally, and it should be produced in standard gauge such as 0.001 in., 0.0015 in., 0.002 in., 0.0025 in., etc.
6. In the case of tubular film, the layflat width of the finished product should conform to commercial tolerances.
7. The film must be issued in reasonably tight rolls, free from folds and wrinkles, and the product must lie flat when it is unwound.

THE EXTRUSION SYSTEMS

Tubular film, as its name suggests, is produced as a seamless tube and is particularly convenient for the manufacture of bags and drum linings, etc., where it is only necessary to cut to length and seal one end. The tubular film extrusion process, however, is limited in the possible output in lb/hour—particularly as regards the smaller sizes such as 2 in. to 6 in.—by the rate at which the product can be cooled and handled. Extrusion machines of small and medium screw diameters, such as 1½ in. to 3 in., depending on product size, are therefore most frequently used for the production of tubular film.

Flat film on the other hand suffers from no such output limitations, and larger machines such as 4½ in., 6 in. or even 8 in. screw diameter are used for this product. Also, because of the type of die necessary for the production of flat film, the use of larger machines is usually found to be essential.

Because of the economic considerations of the above points, it would seem possible that the manufacture of polythene film in tubular form will gradually become less important, and that flat film will in time be utilized for all polythene packaging applications. At one time this view was strongly held in the trade, but to date there have been no signs of this and the demand for both types of film continues to grow at an almost equal rate. It is now felt, therefore, that tubular film will always remain an important packaging medium. Although there are excellent machines in existence, which will automatically manufacture bags in all sizes at high production rates from flat film, the fact remains that such bags can never be as neat, and the process can never be as simple and convenient as is possible by the use of tubular film. Some manufacturers have carefully considered the economics of the extrusion of polythene films of both types, and have found that by installing a number of small machines for tubular film, under the control of one or two

EXTRUSION OF TUBULAR AND FLAT FILM

operators only, it is possible to approach the production rates and economics of flat film at approximately similar capital outlay.

Layout for flat film

Fig. 18.1 shows a schematic layout of the extrusion system for polythene flat film. It will be seen that the process consists of an extrusion machine to which is attached a slit die with adjustable jaws—which may be up to 100 in. or more, in length, a cooling bath with a submerged guide roll, and a take-off consisting of two pairs of nip rolls with rotary edge trimming knives interposed between them. The homogeneous polythene

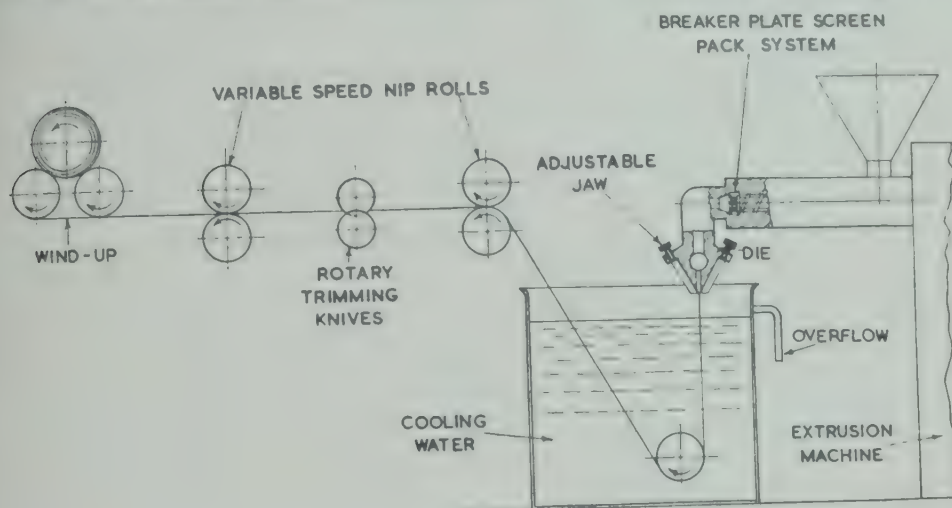


Fig. 18.1. Schematic arrangement of extrusion system for flat film

melt from the extrusion screw, passes through the breaker plate screen pack system, and thence, via the 90° angular attachment piece to the reservoir of the horizontally arranged, manifold-type slit die. It then passes to the die orifice whose adjustable jaws are set to give an extrudate of approximately 0.025 in. in thickness. From this point the product is drawn away from the die orifice by means of the nip roll take-off, at a rate accurately controlled to give a film of required thickness. The film is thus set up to the final dimensions by immersion in water and then passes, via the edge trimmers, to the wind-up where it is rolled on 3 in. cores to a finished roll diameter of between 8 in. and 10 in.

In the process briefly described above, it can be seen that the only size controls available are the length of the extrusion die jaws, which determine the overall width of the product, and the speed of take-off which controls its thickness. Loss in width, due to draw-down and edge trimming, is usually in the neighbourhood of 10%, and the die jaws are made that much longer to compensate for this loss. Intermediate and narrow width films are usually obtained by subsequent slitting operations.

The flat film process may be varied in a number of ways according to the personal preferences and previous experience of the individual manufacturer. For example: the extrusion die can be attached to the machine so that end, rather than centre, feeding is used. Again, the die can

still be used with centre feed, but be arranged in line with the extrusion machine so that part of it is below the machine barrel. And the itself may take a number of different forms.

From an extrusion point of view there seems to be no advantage either way in any of these variations, as excellent film is in commercial production with all of them. But, as with all extrusion processes, the system which works best is the one with which the particular operator has the most experience; and this often leads to unsatisfactory controversial discussions in respect of the merits of one system over another, based on experience of the one system only.

For very long dies, where a considerable pressure drop could be anticipated, it would seem that centre feed has a slight advantage over dies with end feed, and the system, whereby a centre feed die is in line with and partly below the machine barrel, requires the least floor area. On the other hand, many extrusion machines are constructed with their barrels completely enclosed, or supported in the body of the machine—otherwise obstructed—so that such die arrangements are not easily possible.

Another variation of the flat film process dispenses with the water bath, and cools the product by means of a large diameter water cooled casting drum in much the same way as in the process used for the continuous manufacture of polythene/paper laminates described in another chapter.* This method avoids the risk of marking of the product due to disturbances of the cooling water surface, and may be capable of giving a good finish. It is felt, however, that the outputs possible by this means would not approach those obtainable when direct water cooling is used.

Layout for tubular film

A schematic diagram of the equipment used for the manufacture of tubular film is shown in Fig. 18.2. Here the extrusion machine is equipped with an annular die of suitable size, adjusted to give a tubular extrudate of approximately 0.025 in. wall thickness and provided with a passage for inflating air via the die mandrel.

The cooling system, which may be one of the many different possible types, is usually adjustable in its position relative to the extrusion die, and the take-off consists of a series of guide rolls converging finally onto a pair of nip rolls which draw the tubular film at controlled speed from the extrusion die.

The wind-up can be of the climbing batch type as shown, or it can be constructed for centre drive using friction clutches or any of the other well known constant tension systems. The wind-up operation can be carried out directly from the take-off nip rolls as shown, or the product can be returned to floor level.

In principle the tubular film process consists of extruding a tube of specified diameter and wall thickness, and drawing and stretching this

* See Chapter 21.

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tube whilst in the molten state over a floating mandrel of air under slight pressure. Size adjustment, therefore, consists of decreasing or increasing the size of this mandrel—i.e. by extracting or admitting more air—whilst thickness control is given by the speed of draw-off from the extrusion die relative to the speed of extrusion. The inflated tube is set to size by the cooling system, and the cylindrical bubble is continuously deformed into the layflat form by the action of the guide rolls operating in conjunction with the nip rolls, which also serve to seal the tube against loss of inflating air and consequent reduction in bubble size and layflat width.

The arrangement as shown in Fig. 18.2, although possibly the most commonly used form, may be modified in many ways. For example:

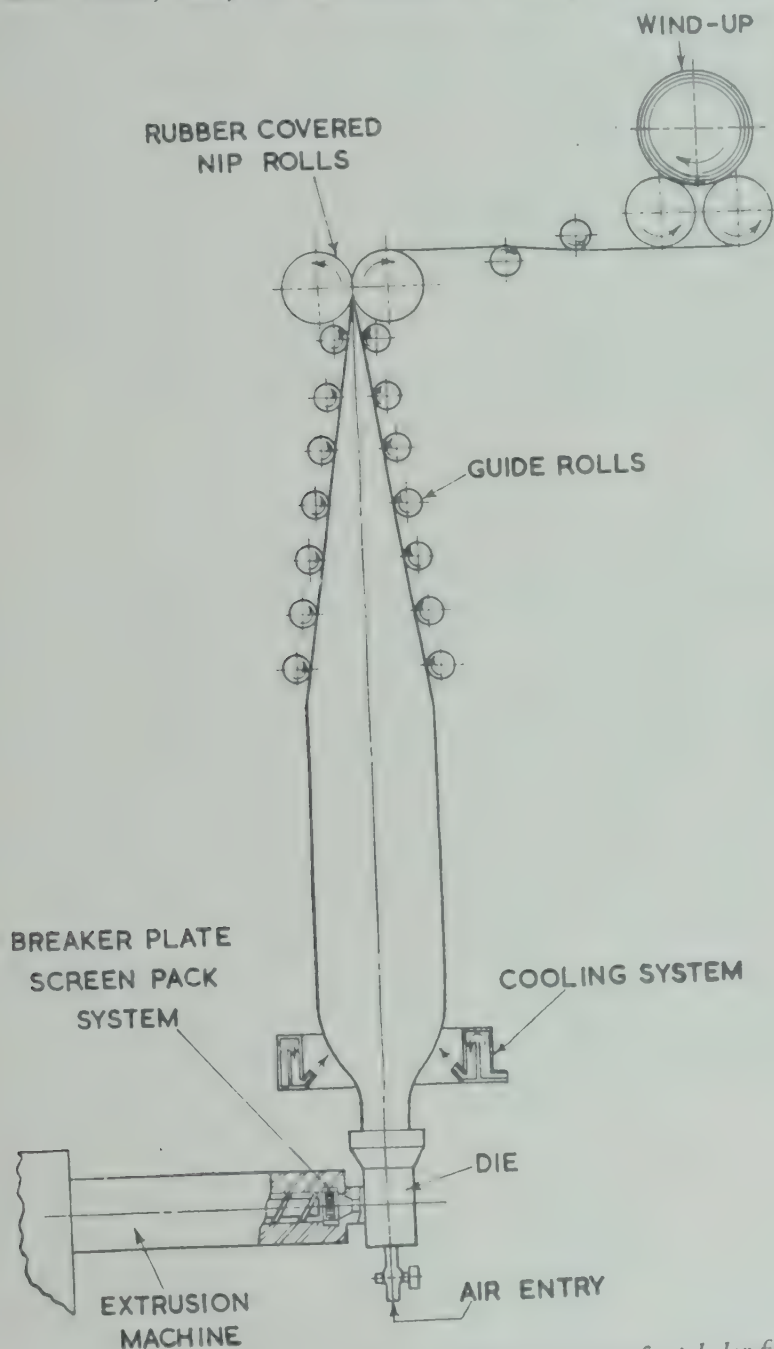


Fig. 18.2. Schematic arrangement of extrusion system for tubular film

the tubular film may be produced downwards, which gives considerable advantage in starting the operation, Plate 18.1, or a horizontal system may be used, which is also very convenient as all the equipment is more accessible for adjustment. On the other hand, each method has its own disadvantages. In the downward system the weight of the tubular product may introduce difficulties, and the air from the cooling system could be expected to have a chilling effect on the die orifice. If the tube is produced horizontally, the effects of gravity must also be taken into account; although with such a thin and light product, and under tension, these effects would be very small.

The upward method would seem to have the slight advantage over the others when once the operation is under way, and certainly is more convenient from engineering and operational points of view.

Recommended extrusion conditions for polythene tubular and flat film are given in Table 18.1.

Having now discussed the two processes for the production of polythene film in a general way, it is possible to proceed with a more detailed description of the various pieces of equipment which are used:

Film quality—whether it be of the flat or of the tubular variety—is controlled by the following factors, which will form convenient headings for individual description: raw material properties; the extrusion machine; die design and construction; the cooling system; the take-off and wind-up.

RAW MATERIAL PROPERTIES

Polythene is composed of a mixture of polymers of varying molecular weights or grades with indeterminate small proportions of polymers of very high and very low melt indexes. If the grade variation is too wide and the material has not been well homogenized prior to extrusion, then the extrudate will contain a number of incompletely melted particles, each of which will show up in the film as an unsightly "blob" or "fish-

Table 18.1. RECOMMENDED EXTRUSION CONDITIONS FOR POLYTHENE FILM

	Tubular film		Flat film	
	Alkathene 7F	Alkathene 2F	Alkathene 7F	Alkathene 2F
<i>Temperatures °C</i>				
Barrel	130	130	140	150
"	135	135	160	165
"	135	140	175	180
Head	140	145	185	200
Die	140-155	155-170	200-240	220-275
Screen pack	40/100/200/ 100/40	40/100/200/ 100/40	40/100/200/ 200/100/40	40/100/200/ 200/100/40
Die gap	0.025 in.	0.025 in.	0.020 in.	0.020 in.
Melt °C	150	165	225	250

eye". This effect can be overcome to some extent by correct extrusion screw design, and by the use of a suitable screen pack system; but it is very difficult by this means alone to eliminate entirely those "fish-eyes" resulting from the use of an unsuitable polythene. This effect is an obvious and easily detected trouble. There are other troubles, however, which can result from the same cause, and which are not so obvious.

Because of its particular method of manufacture, involving the uniform inflation and subsequent collapsing of a very thin walled tube, the tubular film process is extremely sensitive to changes in melt viscosity. If the melt index variation of the polythene being used is such that it varies from particle to particle, it is possible for the viscosity of the melt, as it extrudes from the annular die orifice, to change erratically from point to point in the annulus. Under such conditions the tubular film process becomes very difficult—if not impossible—to operate.

The raw material manufacturers have recognized these difficulties, and now produce melt indexes specially suitable for film production. If possible, one or other of these special types should always be used.

Another advantage of using a correct film type is that good transparency in the finished product is usually obtained with less difficulty; although some users have developed mixtures of polythene with waxes and other materials for this purpose¹ and have also devised methods of improving transparency etc., by some form of after treatment.²

Before leaving this question, it is well to point out that the ill effects referred to as resulting from the use of an unsuitable raw material, can also result from a number of other causes, such as unsuitable extruding conditions, incorrect screw or die design, etc. It is essential to select a suitable raw material for polythene film extrusion, but this does not reduce in any way the necessity for ensuring that the other requirements for good extrusion are also satisfied.

Another factor which may, in time, have its influence on the polythene film picture, is the advent of the high density materials. These highly crystalline polythenes have useful properties which could be valuable in packaging films, for special purposes. On the other hand, their greater hardness and consequent lower flexibility detracts somewhat from the comparative elegance of films prepared from them. Added to this, there is the greater difficulty of extrusion which will be much in evidence in film processes.

At the time of writing, little or no work has yet been published on the extrusion of high density polythenes into packaging films, and this part of the chapter therefore, deals entirely with the manufacture of films from the high pressure materials.

THE EXTRUSION MACHINE

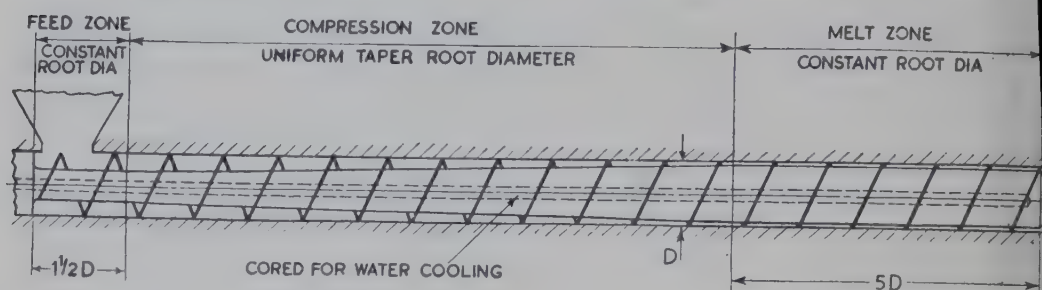
Extrusion machine characteristics for the handling of polythene have been treated in considerable detail in Chapter 17. Very little remains to be said, therefore, on this aspect of film extrusion, except perhaps to

underline, once more, the importance of obtaining a good homogeneous melt at a suitable operating temperature.

Single screw machines of all types, and multi screws have been successfully for this work, and the usual operating method is to increase the number and fineness of the gauze screens in the screen pack until sufficient back pressure is given to ensure the necessary homogeneity.

This method of controlling the back pressure is essential to a varying degree with all existing types of extrusion machines, and a measure of efficacy, or otherwise, of a particular machine or screw for film extrusion is given by the small or large amount of screen pack restriction necessary to ensure a melt of the required characteristics.

Extrusion machines equipped with short, deeply cut screws, and most types of multi screw machines will require a large amount of restriction of this type, and their outputs may suffer in consequence. Machines with long screws but with low compression ratios—i.e. 2 : 1 and the



L/D RATIO 15/1: HELIX ANGLE 25°: COMPRESSION RATIO 5/1: RADIAL SCREW CLEARANCE .005"

Fig. 18.3. Long-type screw for polythene film extrusion

abouts—will also require similar treatment, and again, not be expected to give optimum outputs.

The most important feature of a screw for polythene film extrusion seems to be the compression ratio. If this is adequate, it is possible to ensure a degree of internal frictional working of the material, sufficient to give the required homogeneous melt without undue screen pack restriction and consequent loss of output.

In the previous description* of an extrusion screw for the production of tubes, and profiles, a compression ratio of 3 : 1 was given as a minimum figure. Such a screw, whilst being capable of reasonable film production, would not be considered ideal for this work. Its characteristic would not be flat enough and considerable screen pack restriction would still be necessary.

A more suitable compression ratio would be 5 : 1, and a diagrammatic representation of such a screw is shown in Fig. 18.3. The design of the experimental screw shown in Plate 15.2, was based on the requirements which have been outlined.

Although for high outputs, a length/diameter ratio of at least 15 : 1 is desirable in order to give sufficient heat transfer area for conducted

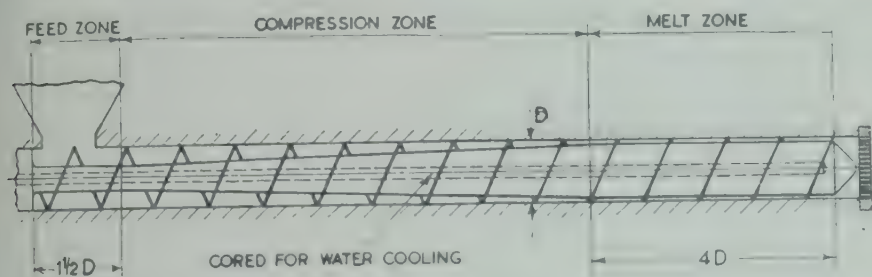
*Chapter 17, p. 328.

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heat, it is still possible to obtain good outputs of homogeneous polythene melts from a shorter screw—e.g. 12 : 1, provided the compression ratio is sufficiently high, and provided that ample motor power is available to drive the high compression screw at high speed, and thus to develop the required extra work heat. It must be borne in mind however, that good regularity of output, i.e. freedom from pulsation is more difficult to obtain with short screws.

A diagram of a short screw of this type is shown in Fig. 18.4, and it will be seen that the compression section—giving a 6 : 1 ratio—is quite short so that the pressure gradient is rather steep. As previously stated, this screw should be run at high speed, and will require rather higher than normal drive motor power.

In designing film extrusion screws of this type, a definite limitation is given by the strength of the steels available for the purpose. All screws require to be bored for water cooling, or controlled heating, in order to give a degree of control to the steepness of the pressure gradient.



L/D RATIO 12/1: HELIX ANGLE 25°: COMPRESSION RATIO 6/1: RADIAL SCREW CLEARANCE .005"

Fig. 18.4. Short-type screw for polythene film extrusion

When, therefore, an extra high compression ratio is required on a screw of small diameter, the thickness of metal remaining at the feed section root can become insufficient to withstand the considerable torque developed when working under near adiabatic conditions. This point must be carefully watched, and in general it is not usually possible to design an ideal screw for the smaller sizes of machine.

DIES FOR THE EXTRUSION OF FILM

The rules and recommendations previously given for the design and construction of dies for the extrusion of thick walled tube and other polythene products of a similar type, apply with even more force to dies for film extrusion. Whether it be flat or tubular film, the final appearance and quality of the product depend very much on the perfection of the die, as does the achievement of the trouble-free, long runs which are so necessary for economic production.

Such important matters as freedom from pockets and shoulders where material can accumulate, attention to the streamlining of all obstructions, and the gradual build up of pressure towards the die annulus etc., have been pointed out many times, and obviously must receive most careful

attention, as all local variations in flow within the die will show up in film as unsightly streaks or bands.

Of equal, or greater importance in the design of film dies is the general robustness of construction. The pressure developed in these dies, particularly in the case of the larger types—may be considerable, and as the dies are usually of cross-head form, these pressures are unbalanced in some position in the flow path. The construction of the dies must be such, therefore, that no suspicion of bending or flexing occurs in the jaws of a flat die; or particularly in the mandrel of a tubular film die under the worst running conditions. If this precaution is not carefully observed, it will be found impossible to obtain a uniform product at a constant gauge.

Another important die constructional feature, which has been previously discussed, but which it will be worth while to re-emphasize here is the arrangement and strength of the thickness adjustment screws in the case of flat film; or of the concentricity adjusting screw for the tubular product. The effectiveness of the adjustments obtained with these screws is important in the extrusion of ordinary tube, but with film where thickness control to an accuracy of ± 0.00025 in. at least, is required, this feature calls for very special attention.

Flat film dies

A photograph of one form of flat film die, with one end cap removed, is shown in Plate 18.2. It is seen to consist of a long steel body of substantially circular cross section, which is machined out longitudinally to form a flow path and reservoir. A slotted deformable adjustment jaw, which extends for the length of the die, is also provided, and the land length allowed for on this jaw and on its fixed counterpart, is usually in the neighbourhood of $\frac{3}{8}$ in. The extremities of the steel body are closed by means of accurately fitting end caps so that no leakage occurs, and the whole is heated by a number of electrical band heaters which embrace as much as possible of the circumference of the die body without obstructing the jaw adjustment screws.

The band heaters are thermostatically controlled in a number of zones—up to as many as 14 on a long die—so that accurate temperature control can be obtained throughout the length of the die, and the number of such zones is dependent on the die length. The die in this case is connected to the extrusion machine by means of a straight through attachment piece, which is also separately heated and temperature controlled.

In the operation of a die of this type the deformable jaw is first set with feeler gauges to give a parallel orifice of approximately 0.025 in., the curtain of polythene in them is allowed to extrude and is passed to the take-off and wind up system via the water bath. Trial pieces are cut from the finished product, and carefully measured for thickness variation. Any necessary adjustments are then made by means of the deformable jaw which may be slightly bent locally to control thick or

thin bands, and by temperature control of individual parts of the die length.

In more ambitious set ups, recording instruments are provided at a number of suitable points in the film width, so that a continuous record of local film thickness variation is given. Such a system makes for easy thickness adjustment against a visual indicator, and gives an accurate control of dimensional uniformity.

There are a number of other successful designs of flat film dies, which vary in detail from the type shown in Plate 18.2. Some are provided with one adjustment jaw which is moved bodily in a horizontal direction rather than obtaining adjustment by deformation, whilst others use two movable jaws, each set at an angle of 45° or thereabouts from the vertical. Each of these designs has its own particular advantages and drawbacks. In the design shown, for example, there may be a tendency for uncontrollable deformation of the adjustable jaw, due to the effects of heat. On the other hand, the actual adjustment of the jaw on this design is often more effective, and the risk of material leakage is less.

Tubular film dies

Extrusion dies for the production of flat film call for difficult and very accurate machining of long lengths of hard steels. Dies for tubular film, on the other hand, are much simpler to construct, although equal accuracy and care is necessary. Another difference in the two film processes, from die considerations, is that, whilst with flat film one die size only is necessary in the most economic production set-up, the tubular film process uses a number of sizes.

It will be noticed in Table 18.1 that the recommended die temperatures for flat film are much higher than those for the tubular product. This difference is necessitated by the different natures of the two processes; it being impossible to control and handle tubular film at the same high material temperature which is found to be the best for flat film. Tubular film therefore, is drawn—by the take-off—at a relatively low temperature where complete relaxation is impossible, so that considerable orientation occurs. As it is drawn, in addition to being inflated, this orientation may take place longitudinally as well as laterally. It can be seen that the ratio of lateral to longitudinal orientation, and thus the relative strengths of the film in the two directions, is dependent on the amount of longitudinal draw relative to the lateral inflation. A considerable range of diverse characteristics can be given to the tubular product by intelligent variation of these two factors, but for general use it is desirable for the film strength to be equal in both directions. Under ideal conditions this would call for a number of dies, or at least interchangeable die parts, so that the die annulus width, or the die diameter, can be adapted to suit the speed of longitudinal draw.

A compromise is usually adopted, however, and it has been found that working under average conditions, and with a 0.025 in. annular gap, a blow ratio of bubble diameter to die diameter of 2 : 1 gives approximately

the desired characteristics. Empirically, if a blow ratio greater than this is required, then the die annulus should be opened to allow a greater speed of draw, and vice versa.

There is another matter, important from the point of view of production, which sets a practical limit to the blow ratio which may be used. It has been previously pointed out that the tubular film process works by

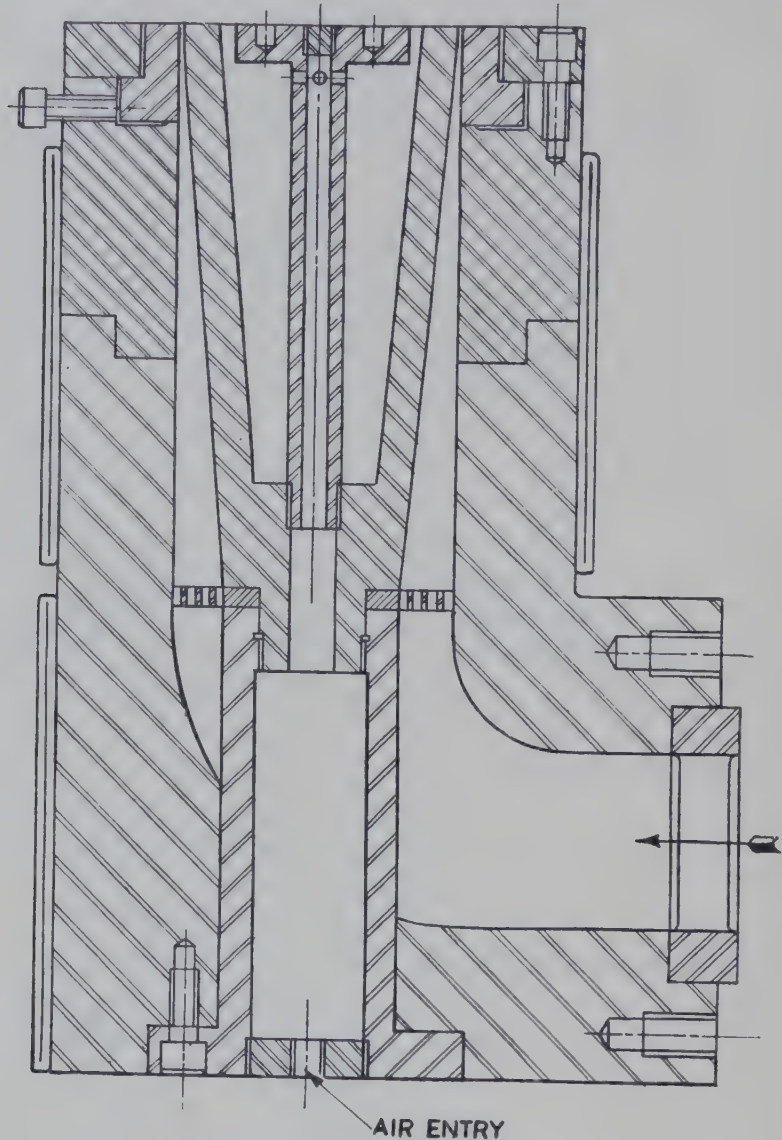


Fig. 18.5. Typical die for small and medium size tubular film

drawing a tube of polythene over a floating mandrel of air and continuously deforming this bubble into the flat form by means of nip rolls. If the various distances from the die orifice to the nip rolls are calculated, embracing the extremities of the layflat width between the rolls, it will be seen that the length of the film path varies considerably from point to point in the circumference of the bubble. It will also be seen that this variation increases with the blow ratio. This means that the tension on the tubular film, due to the action of the nip rolls, is not uniform at all points around the circumference, and is greatest at the extremities of the

flat width, or thereabouts. Irregular draw of this kind has a great tendency to produce creases and folds in the film, and this tendency obviously must increase with the amount of inflation. It has been found that a blow ratio up to about 2.5 : 1 in the smaller sizes, and 1.5 : 1 or 2 : 1 in the larger sizes, should not therefore be exceeded. Two sizes of tubular film extrusion die are shown in Figs. 18.5 and 18.6.

They are seen to be of essentially cross head form, and the largest one is arranged as an adaption of the smaller size by means of an interchangeable mandrel and outer die. Such an arrangement is often convenient in production, as it allows for size changes with the minimum of

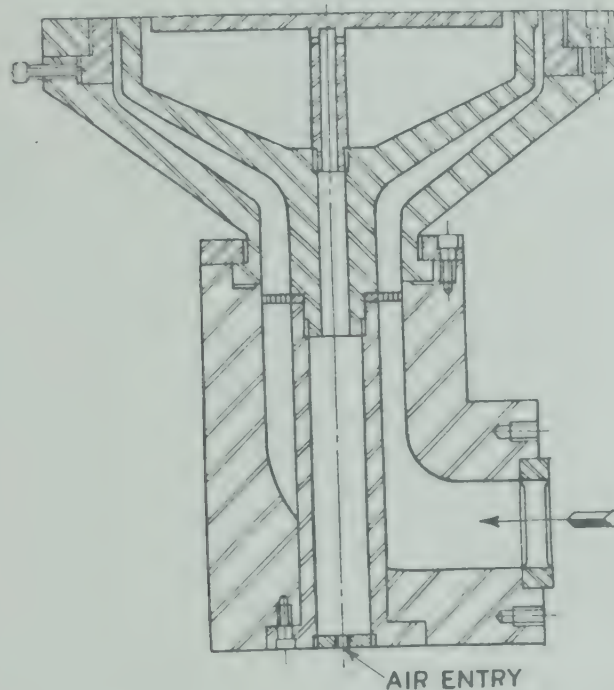


Fig. 18.6. Adaption of die shown in Fig. 18.5 for large size tubular film

dismantling and consequent loss of heat and material. The die annulus is set at about 0.025 in. in both cases, and the land length at $\frac{3}{64}$ in.

An interesting feature of the dies shown, is the provision of a second breaker plate screen pack, which is arranged in ring form around the die mandrel. The purpose of this is to neutralize the pressure differences which are set up by the right angle feed to the die, and to give extra support to the die mandrel at the point where pressure differences can occur. Otherwise, both dies follow roughly conventional pattern and require no further description.

Tubular film dies are capable of considerable variation of design, the principal aim being to provide uniform flow to the die land and exact adjustment of extrudate thickness at the die orifice. Some designs seek to reach the first of these objectives by creating turbulence in the melt during its passage from the right angle to the die land; whilst others use a mandrel which is set eccentrically within the die body. In the horizontal method of tubular film production, difficulties due to the use of

a die of cross head form can be avoided but spider line trouble then becomes important. In such systems, therefore, the cross head type die is still sometimes used—although dies of the offset type are usually preferred.

Another type of tubular film die utilizes a central feed of melt (Fig. 18.7) so that the pressures are uniformly distributed around the mandrel. Such a die of course, follows normal tube die practice, as is used in horizontal extrusion and, therefore, gives difficulty again with spider lines.

However, it is possible to obtain a good product with all these different die types, provided the dies are designed according to the dimensional recommendations given in previous parts of this chapter, and provided the extrusion conditions are suited to the particular design.

The problem of obtaining accurate extrudate thickness adjustment is a difficult one, and is in part dependent on uniform pressure distribution

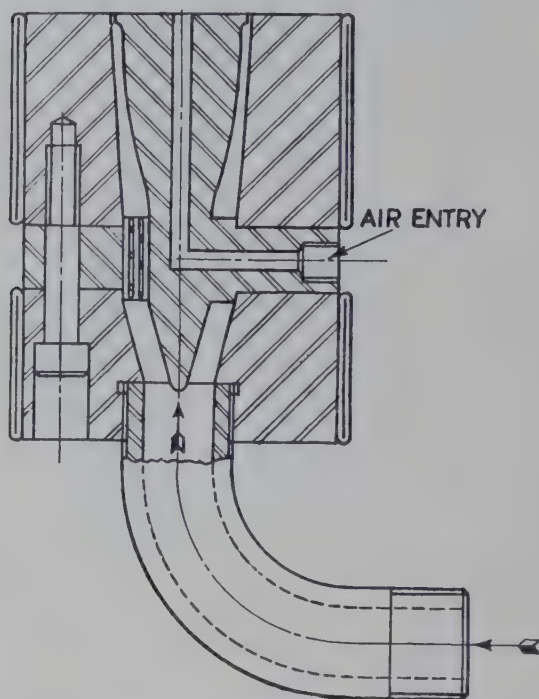
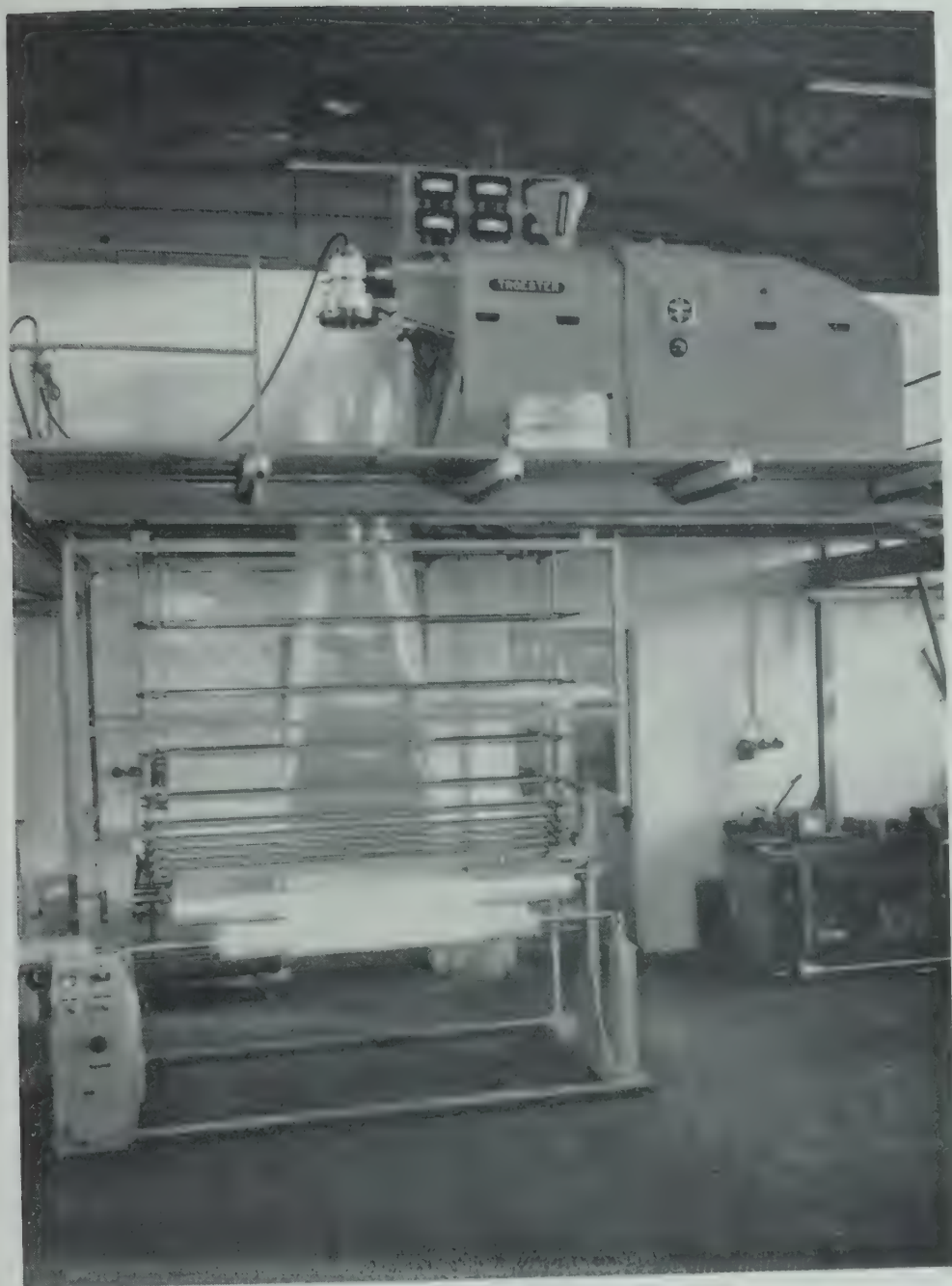


Fig. 18.7. Tubular film die with centre feed

in the die body. If this is not good, it is possible to obtain an extrudate of reasonably uniform thickness when setting up at low output rates, only to find on speeding up for production that the adjustment has been disturbed. It is extremely difficult and uneconomical to run with such a die, because any change of extruding conditions necessitated by production requirements will also bring about alteration in pressure distribution, and thus in the extrudate thickness and uniformity.

The importance of the die design from this aspect therefore, cannot be over emphasized. Many different views have been expressed regarding the best system of final die concentricity adjustment, all of which seem to have points for and against. A common method uses 4 or 8 screws for moving the outer adjustment ring bodily. This however, gives no



*Plate 18.1. Downward extrusion of tubular film
(Courtesy Paul Troester, Hannover-Wulfel)*

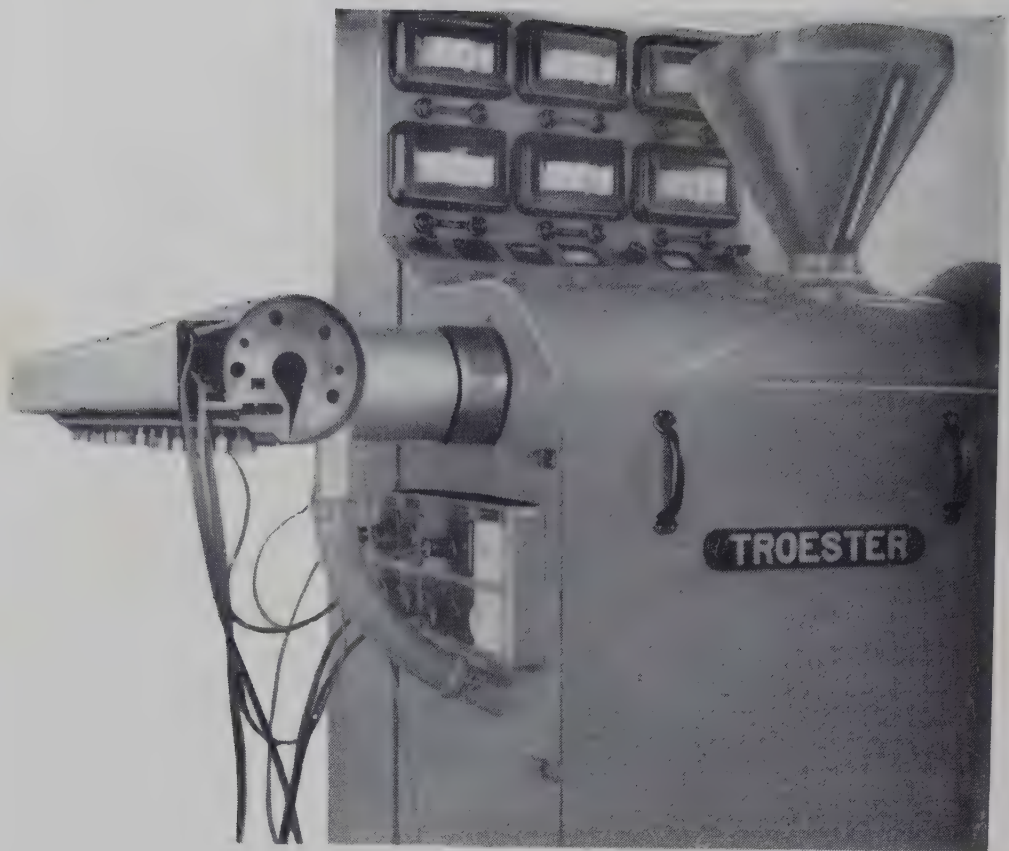


Plate 18.2. One form of flat film die (Courtesy Paul Troester, Hannover-Wulfel)

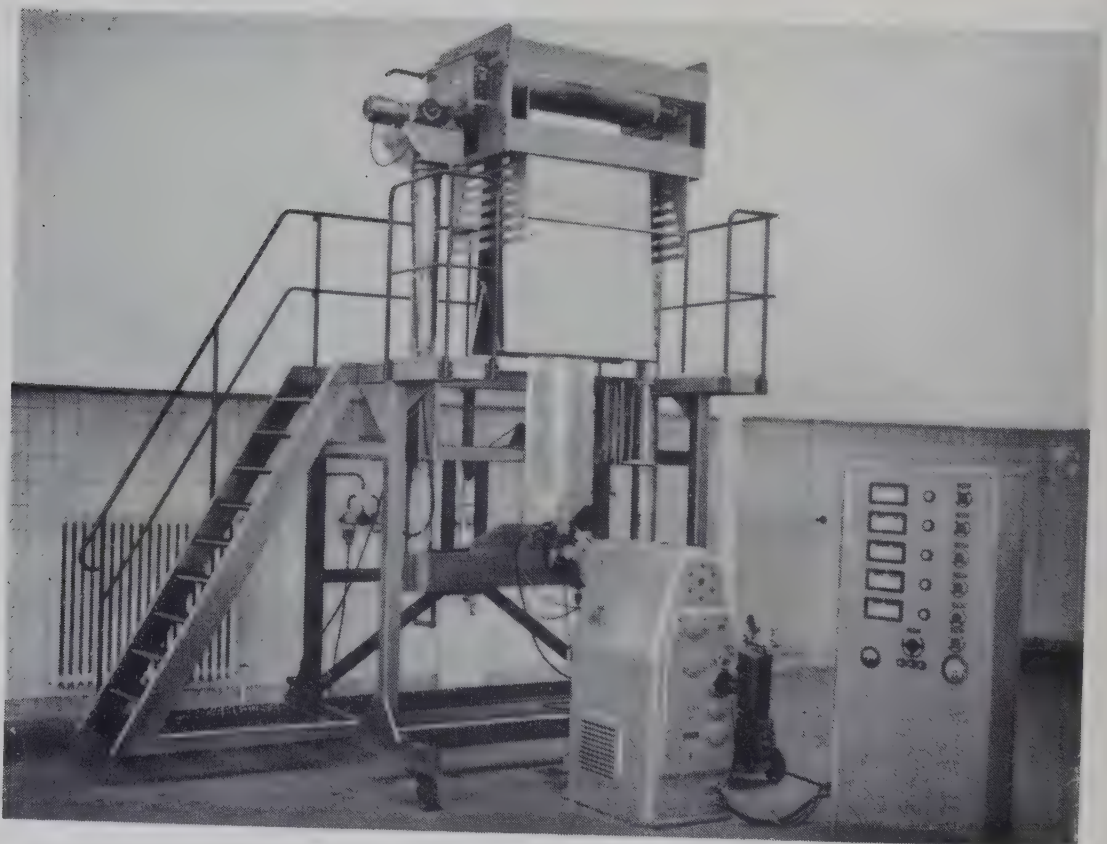


Plate 18.3. Tubular film deformation system in which guide rolls are not used (Courtesy A. Reifenhauser, Troisdorf)

control over local thick or thin bands which often seem to occur, and in order to overcome this limitation, a large number of screws set at small centre distances have been used, and rely on giving small local deformation to the adjustment ring. This system has been taken a stage further in one case³ where a very thin and easily deformable ring is used in a special way. Another interesting method provides a number of pockets spaced around the extrusion orifice, each pocket being arranged for feeding with a cooling, or alternatively a heating, medium, and attempts to achieve thickness uniformity by controlled local changes of temperature around the die orifice.⁴ Other systems rely on obtaining reasonably uniform thickness at the die orifice, and then completing the adjustment by means of differential control to the bubble cooling system.⁵

FILM COOLING SYSTEMS

The cooling systems used for the two types of film, are seen in a diagrammatic form in Fig. 18.1 and Fig. 18.2, and have been briefly referred to earlier.

It will be seen that flat film utilizes a water bath with one or more submerged guide rollers. The height of this water bath is adjustable so that the distance between the die orifice and the water surface, i.e.—the hot stretch distance—is controllable between about 1 in. and 9 in. It has been found in practice, that variation of this hot stretch distance can have a considerable effect on the film properties and on its ease of production. Another variable which can have a great effect on the ease of producing a crease-free film with good properties, is the temperature of the cooling water, and ideally this also should be controlled. The effect of these and other variables have been fully treated in a previous publication.⁶

The cooling system for the production of tubular film is, because of the nature of the process, somewhat more critical than that used for flat film and, therefore, requires a more detailed description.

It has been previously pointed out in Table 18.1 and subsequently, that the melt temperature found to be the most suitable for the production of tubular film is relatively low. The degree of chilling required to set up a thin film therefore, will not be high and no artificial cooling system is necessary when operating at low production speeds. Immediately an attempt is made to speed up and obtain economic production rates, however, certain difficulties arise.

The first of these difficulties to be noticed, is that the inflation point—i.e. the lowest extremity of the bubble—increases its distance from the die. If this effect is allowed to continue a second bubble may commence to form immediately above the die, and this will propagate itself when it passes through the nip rolls thus giving, in effect, a string of sausages! A second, and equally serious difficulty is that the product adheres to itself between the nip rolls and is, therefore, no longer tubular. It will also tend to stick to the rolls themselves, so that production, even of this useless product, quickly becomes impossible. As the output increases

therefore, artificial cooling of the bubble must be provided so that point of formation remains constant, irrespective of speed or temperature. And it is emphasized that the effectiveness of the method used is a probably one of the most important requirements in the whole tubular film process.

To appreciate this statement, it must be remembered that the polythene extrudate comes from the die in a molten state, so that it can be very easily deflected, inflated and distorted by any influences which are applied to it. If the cooling system is such that more cooling—even the smallest degree more—is applied at one point only, then the film will solidify more quickly at that point and will not inflate further. The tubular film will, however, continue to inflate at other points where cooling is not so effective. Thus, the film will be thick where the extrusion cooling has been applied, and will also be at greater tension due to uniform pulling by the nip rolls, so that creases will almost inevitably occur.

Much experimental work has been carried out on the development of systems to provide uniform cooling in the tubular film process, and many of these form the subject of patents.^{7, 8, 9, 10}

TAKE-OFF AND WIND-UP SYSTEMS

A general idea of the arrangement of take-off and wind-up units is clearly given in Figs. 18.1 and 18.2. Taking the flat film process first, the take-off system follows orthodox web handling practice, and there is little which would require special description. The assembly must be constructed as a semi-portable unit so that it can be easily pushed away in order to facilitate die removal and extrusion machine cleaning. The first pair of nip rolls which may have to be water cooled should be as close as possible to the water bath, and long unsupported runs of film must be avoided. Crease formation can be prevented by making sure that there is no undue longitudinal tension on the product between the two pairs of nip rolls, and between the last pair and the wind-up. For this reason, the second nip rolls are replaced in some assemblies by three rolls in pyramid formation, and the wind-up is relied upon to give tension sufficient for edge trimming. The use of convex flexible rolls, placed at strategic points, will also contribute much to the production of crease-free film.

Take-off for tubular film

The take-off systems for the production of tubular film is somewhat more complicated, and in consequence possesses a number of features which require special treatment. In these features, the extrusion die, the cooling systems and the take-off, are all directly concerned and interdependent. For any tubular film take-off to function correctly—i.e. to produce a good coil of layflat material which is free from creases and localized high spots—the die, in conjunction with the cooling system, must provide an inflated tube which is uniform in wall thickness to fine limits, and is symmetrical about the die/nip roll centre line. If adequate

EXTRUSION OF TUBULAR AND FLAT FILM

attention is given to these points, then most of the crease forming influences will have been removed and the working of the take-off itself will become a less difficult matter.

The tubular film take-off consists basically of two parts, i.e. the nip rolls and the deformation system, and the functioning of these parts is identical whether the film is produced vertically upwards, downwards or horizontally. The nip rolls are usually rubber covered and are set so that the pressure is just sufficient to prevent loss of air from the bubble. The greater the distance from the die to the nip rolls, the greater the degree of natural cooling which can be effected on the bubble, and hence the greater the possible output without resorting to a large amount of artificial cooling.

Unfortunately however, the bubble is very sensitive and susceptible to draughts and vibrations, and it is extremely difficult to prevent a very long bubble from wandering with respect to the die and nip. Therefore, the distance between die and nip rolls is often made adjustable so that the optimum position can be found having regard to the degree of artificial cooling and the linear speed of production.

In some systems the bubble is protected by means of a tubular draught screen so that disturbances due to outside influences are minimized; others utilize a deformation system which in itself gives sufficient support and protection.

The deformation system is probably the most troublesome part of any tubular film take-off. Its function is to take the bubble from the cooling member and continuously deform it into a flattened double sheet without introducing creases, puckers or other defects. In order to convert the circular form into the flat, the width of the product must be drawn out to $\pi/2$ times the diameter, and the only force available to do this is the very light internal air pressure of the bubble. Deformation systems, therefore, aim at assisting the action of this small internal pressure by introducing the change of shape so gradually that the stability of the system is not disturbed.

It has been found that two sets of small diameter rolls converging towards the nip at an angle of between 15° and 20° can bring about the desired effect, provided they have no drag on the film. These rolls should be of very light construction, and mounted on pivots, or some other form of low friction bearing. Alternatively, they may be driven at the same peripheral speed as the nip rolls, in which case they may be of more robust construction.

Rolls have a certain disadvantage, in that the support given by them to the film, is discontinuous, causing the converging surfaces of the tubular product to assume a corrugated form. Creases may occur due to this, and some deformation systems therefore, dispense with rolls altogether and use two converging flat surfaces which are constructed from suitable materials so that their drag effects are as low as possible.

In experimenting with boards and other materials for these flat surfaces it has been found that the friction effect, or drag, is least when the surfaces

in contact with the film are rough or broken, and equipment based on principle is successfully used in many production units (Plate 18.3).

Gussetting

Before finally leaving the question of take-off, it will be useful comment briefly on "gusseted" tubular film. A difficulty sometimes occurs in the use of polythene tubular film in that it has a tendency to stick to itself, or "block". Blocking is caused by the film surfaces being pressed together by the nip rolls whilst they are still hot, and although no actual adhesion takes place, a very close contact is given which renders the flattened film extremely difficult to open for use. This blocking effect can be prevented, or at least minimized, by attention to the extrusion conditions; making certain that the film is adequately cooled before it reaches the nip rolls, and using a low die temperature. Its effects on the usefulness of the product can, however, be avoided if the tube is gusseted, i.e. provided with pleats or tucks along diametrically opposite sides, and film manufactured in this form is preferred in a number of packaging applications for this, and for other more obvious reasons.

Gusseted tubular film may be produced continually with the main extrusion operation, by means of additions to the take-off system. The apparatus used may take the form of a pair of wedge shaped blades, which are arranged to form the inwardly projecting tucks, or it can consist of a flattened funnel-like structure with progressive, inwardly projecting portions arranged on diametrically opposite sides. Another method uses a series of small rollers which are mounted on the extremities of a number of adjustable arms arranged to gradually deform the inflated tube in the required manner. Various systems for producing gusseted tubular film form the subject of patents.^{11, 12}

The wind-up

The wind-up is the last part of the process, and no description on polythene film production would be complete without a brief reference to the equipment used.

The method to be adopted will depend very much on the individual manufacturer, and the form in which he wishes to present his products for sale. Both the flat and tubular products are handled in the same way and on similar equipment, so that any features to be observed will be identical to both cases.

It is important always to remember that there must be no long runs of film which are not adequately supported by rolls—if necessary, driven rolls—at frequent intervals. Similarly, there must be no undue longitudinal tension at any point. Another important matter, is the degree of tightness of coiling. It is obvious that a nice tight coil looks very good and is easier to handle and deal with generally. Unfortunately, as previously mentioned, the film made under production conditions frequently contains localized thick bands, due to some irregularity in the

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die or cooling system: these thick spots are quite unimportant as regards the usefulness or otherwise of the film as a packaging medium, and are usually undetectable by eye. In a tightly wound coil, however, they become apparent by the building up with successive layers to form a hoop and, in consequence, cause local cold stretching of the outer layers of film. In order to avoid this effect, therefore, it is always wise to avoid the use of high tension on the wind-up, so that the coil is comparatively loosely wound. On the other hand the coil must not in any circumstances be so loose that it becomes difficult to handle on automatic equipment. Here again therefore, as with so many other features of the film extrusion processes, the ideal is a nicely adjusted compromise.

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CHAPTER 19

INJECTION MOULDING

P. J. MEEKS AND M. Q. TESSIN

POLYTHENE is widely used as an injection moulding material. It has a broad moulding range, excellent flow characteristics, good heat stability, and is not sensitive to moisture. In moulded form, it possesses an outstanding balance of physical properties. These properties permit the use of polythene in a wide variety of applications, including toys, housewares, containers, bottles and industrial parts.

Polythene is injection moulded in conventional equipment, developed to fabricate a wide range of thermoplastic materials. The machines perform the following functions during the moulding operation:

Measure an amount of plastics material either by volume or by weight.
Feed the measured material into a temperature controlled heating cylinder.

Melt the solid material to a liquid state.

Clamp the mould halves together.

Force the liquid through a nozzle into a mould with cavities cut to the desired part shape.

Control the mould filling and cooling times by timer mechanism.

Open the mould halves and eject the moulded part.

Close the mould halves and repeat the cycle—sometimes automatically and more often semi-automatically.

EFFECT OF BASIC PROPERTIES IN MOULDING POLYTHENE

Low density polythene used for injection moulding generally ranges in melt flow index from 0.2 to 20. The polymer viscosity is inversely related to the melt flow index as shown by data in Table 19.1.

Table 19.1. MELT FLOW INDEX VS. MELT VISCOSITY OF POLYTHENE

Melt flow Index	Melt Viscosity ^a (poises at 190°C)
20	3,700
7	7,000
2	18,000
0.7	58,000
0.2	120,000

^a Measured on the Caplastometer.

The higher the melt index, the more fluid the material and the faster the material will fill the injection mould. The more fluid material is widely used for injection moulding. It permits faster cycles due to low temperature and pressure requirements, and possesses physical properties satisfactory for many applications.

Low density polythene is a material with usually about 60% crystallinity. The crystallinity is a dominant property in injection moulding. It has a marked influence on both behaviour of the material during moulding and physical properties of the moulded product. These effects will be discussed in detail later.

FEEDING

Types of feed

Polythene is fed into the injection moulding machine by one of the common methods—volumetric feed, weigh feed and preplasticizing. All three methods measure the amount of material to be injected into the mould but differ in the following ways:

Volumetric feeding, the most widely used, allows granules to drop from the machine hopper and fill a small, variable volume measuring cylinder. The movement of the injection plunger moves the measured volume of granules into the heating cylinder. This device has the advantage of low equipment costs; but, due to the variation in random packing of the granules, the volume of granules may vary in weight. An accurate feeding is therefore impossible, and the machine is usually operated with a larger feed than necessary to fill the mould to compensate for the possibility of running short. The larger zone of unmelted granules in the heating cylinder causes excessive pressure loss during moulding.

In weigh feeding, an improved technique over volumetric feeding, granular material equal to the weight of the part and runners is measured and dropped into the heating cylinder. The weighing system provides better injection pressure control and faster injection speeds by enabling the use of maximum injection pressure without fear of flashing material in the mould.

The preplasticizing feed arrangement consists basically of melting the granules in one cylinder (preplasticizing cylinder) and moving the fluid polymer into a second or injection cylinder. If the injection cylinder is arranged to form a chamber of rigidly fixed volume, the effect is to measure the mould charge very accurately.

Granulation

Three types of polythene granulations commonly are being used commercially: cube cut; cylindrical pellet; spheres (approximately).

The granulations range in apparent density from 0.46 to 0.54 gms./ml. Uniform granulation is extremely important. Feather edges, fines, strings, and sticks (granules of excessive length) are undesirable. All interfere with optimum moulding.

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Due to the waxy surface of polythene, external surface lubrication is not essential, but can be used for one or more of these reasons: reduction of surface friction, compaction of granules or to facilitate pigment dispersion during dry blend colouring. In the latter wetting agents commonly are used—they also may show some action as surface lubricants.

FLOW OF MATERIAL THROUGH THE HEATING CYLINDER

The function of the injection moulding heating cylinder is to melt the granules into a completely fluid state. A conventional heating cylinder is shown in Fig. 19.1. The cylinder should be designed to provide adequate, uniform heating of the granules with as little pressure loss as possible. Material holdup in the cylinder should be avoided since polythene, as are other thermoplastics, is subject to degradation on prolonged exposure to moulding temperatures.

Melting polythene within the heating cylinder depends on: heating cylinder design, and efficiency; crystallinity and thermal properties of

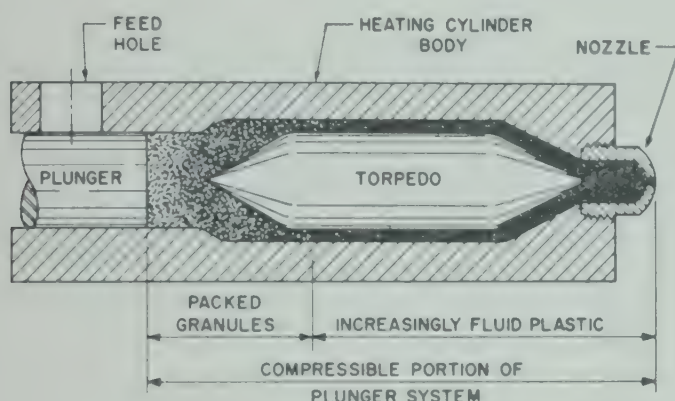


Fig. 19.1. Conventional injection moulding heating cylinder

the polythene; size and shape of the granules; and heating time as controlled by the moulding cycle. A uniform granulation is desired to reduce air entrapment in the heating area and subsequent burning or oxidation of the material. If the granulation is too small in size, burning also may result.

As polythene is melted, its viscosity decreases. There is a significant viscosity change in the melting point area, due to melting of the crystallites. Since polythene is a non-Newtonian polymer, the viscosity of the molten material in the heating cylinder is affected by temperature and by shearing stress.

The variation of viscosity of polythene (melt flow index 2) with temperature is shown in Fig. 19.2. General-purpose polystyrene is included for comparison. The change of viscosity with temperature is less for polythene than polystyrene. This indicates that, once polythene is in the fluid state, the viscosity is less sensitive to temperature. From this it also would appear that polystyrene is a much stiffer flowing polymer

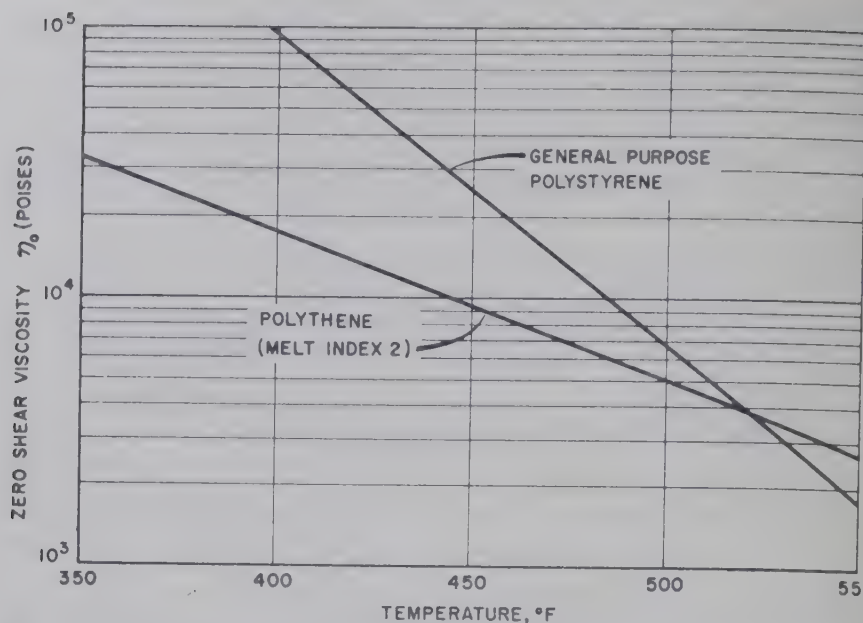


Fig. 19.2. Variation of melt viscosity of low density polythene with temperature

than polythene. But these data were obtained at low pressure and essentially zero shear, while during injection moulding the polymer is under considerable shearing stress. Studies³ indicate that an average shearing stress on the material in an injection moulding machine cylinder during operation at normal pressures is about 700,000 dynes/cm². The effect of this pressure on the flow viscosity of low density materials at recommended moulding temperatures is shown in Table 19.2.

These data show polystyrene is much more sensitive to the effect of shear stress, its melt viscosity having dropped from 24,000 to 1,500 poises. Polythene is more fluid at zero shear, but the melt viscosity does not decrease as markedly as with polystyrene. Thus under these moulding conditions polystyrene is more fluid than melt flow index 2 polythene.

In moulding polythene, conventional injection moulding nozzles are used in most cases. Sometimes, with a high melt flow index polymer, it has been found desirable to introduce a nozzle restriction to increase back pressure. This prevents the passage of unmelted granules or improperly melted material into the mould. It also assists in eliminating surface blemishes in the finished part due to trapped air.

Table 19.2. EFFECT OF SHEARING STRESS ON MELT VISCOSITY⁴

Shearing Stress	Viscosity, poises	
	General purpose polystyrene (moulding temp., 450°F)	Polythene (melt flow index 2) (moulding temp., 450°F)
Zero shear (η_0)	24,000	9,500
700,000 dynes/cm ² (η_7)	1,500	5,300

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Since polythene is basically a mixture of molecular weights, it is necessary to have, in addition to a material of uniform temperature, a material which is, as far as possible, homogeneous. Insufficient mixing would result in non-uniform flow within the polymer as it entered the mould and would definitely influence the properties of the moulding.

BEHAVIOUR INSIDE THE MOULD

The flow of polythene in the mould has been observed using a glass window mould⁵. Motion pictures have been taken of the flow behaviour patterns. Several shots are shown in Plate 19.1. As polythene enters the mould and the material starts to cool, crystallization begins. Crystallization of polythene is extremely rapid⁶; the crystallization induction

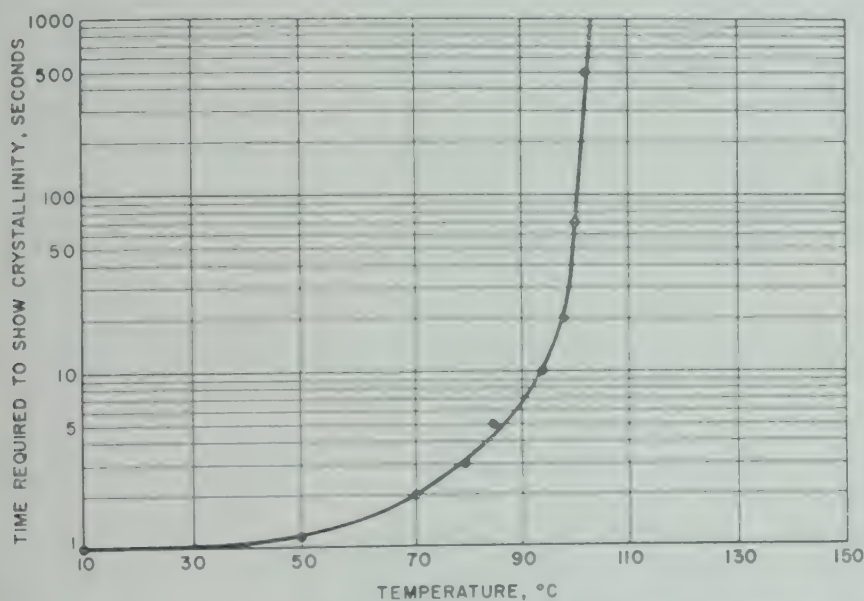


Fig. 19.3. Crystallization induction time of low density polythene (melt flow index 2)

time is very short (Fig. 19.3). Crystallization results in the formulation of a weak front which, upon the effect of pressure from incoming material, breaks up and then tends to reform. The motion pictures on flow of polythene in the mould show several interesting features: (1) Polythene shows a greater tendency to jet when entering the mould than does polystyrene. (2) The moving front eventually overtakes the jet, but the finish of the moulded piece may show surface blemishes where the material in the jet and the plastic front meet and do not weld clearly. (3) As polythene flows into the mould, the curvature of the plastic front does not reverse like polystyrene. This indicates that molten polythene does not wet the mould walls. (4) When polythene is forced against the mould wall and becomes solid, the material does not stop but is scraped along the mould walls in the direction of flow.

If the polymer next to the mould wall can be kept in at least a semi-molten state until flow in the mould ceases, the surface finish is markedly

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improved. This may be done either by high cylinder temperatures (above 450°F or 232°C) or high mould temperatures (above 130°F or 54°C) or a combination of the two. Another method is listed in a du Pont patent, U.S. 2,624,916. This tells that coating the mould for polythene with an insulator will reduce the heat conduction and improve the

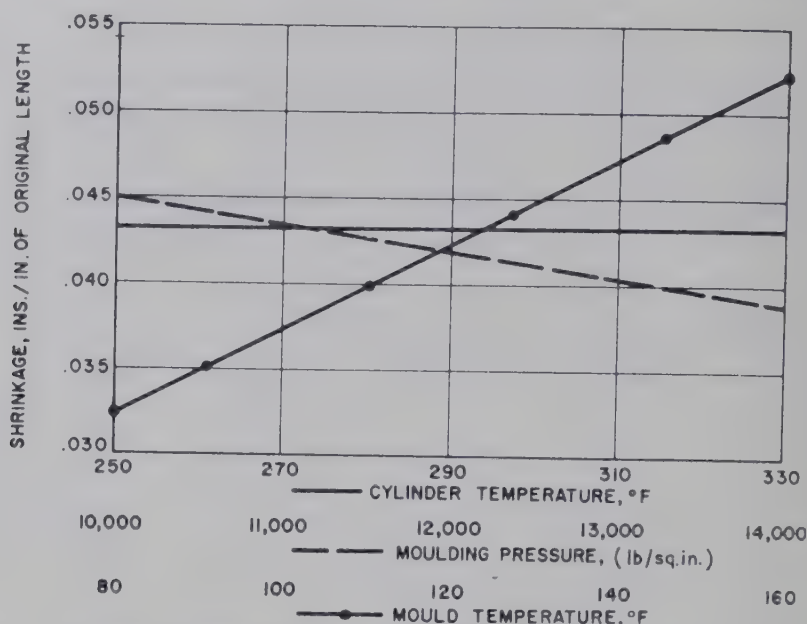


Fig. 19.4. Effect of mould temperature, cylinder temperature and pressure on mould shrinkage of low density polythene (melt flow index 2)

surface finish by permitting the mould to be filled before recrystallization takes place.

The most pronounced improvement in surface gloss is achieved by switching to polymers of higher melt flow index. These materials have lower viscosity, and would be expected to fill the mould faster. The final pressure build-up in the full mould would be more capable of forcing the hotter and less rigid skin to weld together.

High injection pressures would increase the amount of jetting as the material enters the mould. The tendency to jet can be reduced by decreasing the speed of injection or by using lower viscosity materials, i.e., melt flow index 7 or 20. It has been observed that melt flow index 20 material shows much less tendency to jet than melt flow index 2.

From the work with the glass window mould, it appears that very little discharge occurs in the mould when the plunger is withdrawn after the mould is filled. This is in contrast to polystyrene which shows a good deal of discharge depending on mould design. If the plunger is left forward, polymer is packed into the mould as the initial shot shrinks in volume. This packing occurs predominately in the gate area. It may result in improper welding between the initial shot and the packed material, particularly at low mould temperatures. The material must be hot to weld satisfactorily. Poor welds may show up later on as peeling or breaking off of the surface skin at the gate.

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Mould shrinkage is pronounced with polythene and is approximately ten times that encountered with general-purpose polystyrene. Mould shrinkage values from 0.015 inch/inch to 0.050 inch/inch have been observed. The degree of shrinkage depends on moulding conditions, geometry of the mould, and cycle time. The effect of mould temperature, cylinder temperature, and pressure on shrinkage is shown in Fig. 19.4.

MOULD DESIGN

The mould has an important function in the injection moulding process. Moulds are usually designed in one of four basic arrangements: the conventional mould with sprue, runners, and gates (Fig. 19.5); a three-plate mould (Fig. 19.6); a hot runner mould (Fig. 19.7); and a runnerless mould (Fig. 19.8).

In a conventional mould, the material flows from the cylinder nozzle through a sprue and runner into a cavity. Good moulding practice dictates that a restriction or gate be placed at the entrance to the cavity to seal the opening when the cavity is full. The three-plate mould

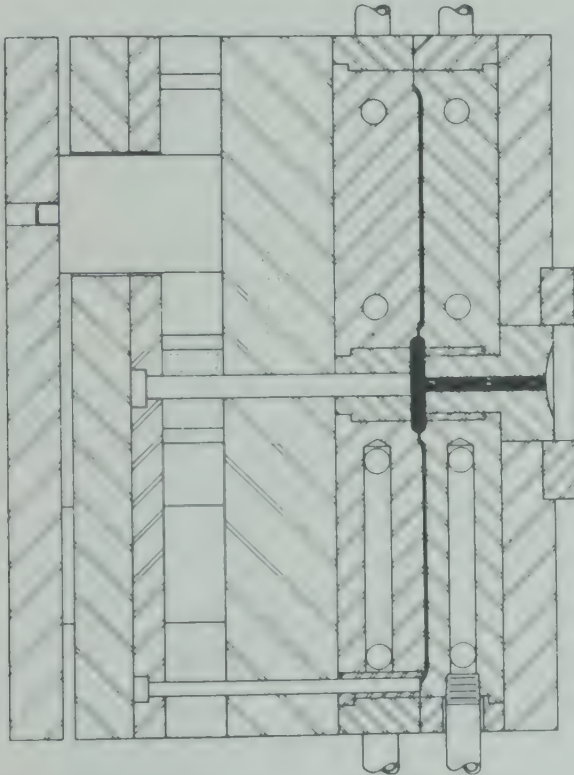


Fig. 19.5. Conventional injection mould

arrangement allows the cavity to be entered from the centre and provides an automatic separation of the runner system from the parts. A hot runner mould is similar to the three-plate mould, except that the material in the runners and sprues is maintained in a liquid state by heaters in the runner block adjacent to the runner system. In the runnerless

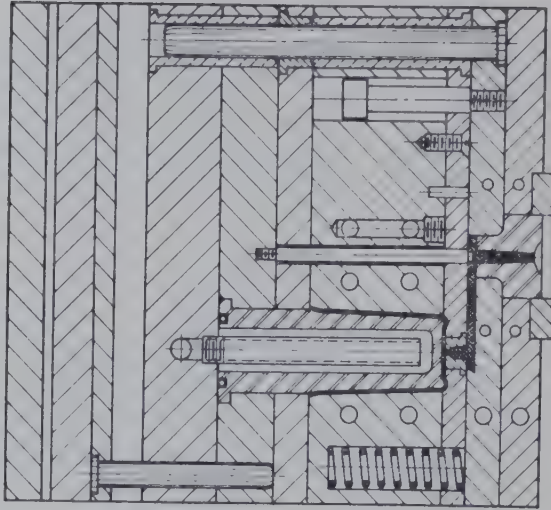


Fig. 19.6. Three-plate mould

mould, the cylinder nozzle is extended into the mould against the cavity opening. A multiple cavity arrangement necessitates a nozzle reaching into each cavity.

Runners, sprues and gate shapes and sizes commonly used with polystyrene⁷ are successfully used in the moulding of polythene. Photographic studies of polythene as it enters the cavity show that this material usually jets through the gate opening. This is especially characteristic of lower melt flow index (stiffer flowing) grades. It is believed that the cool, crystallized front does not have sufficient strength to retain the injection pressure, and that this pressure causes the front to break and material to jet. A wider gate would help to eliminate jetting and the resultant flow marks on the part surface. A large gate, however, increases the time to freeze and may cause excessive packing of material.

The characteristic high shrinkage and flexibility of polythene dictate a need for some basic design features. A positive acting sprue puller is

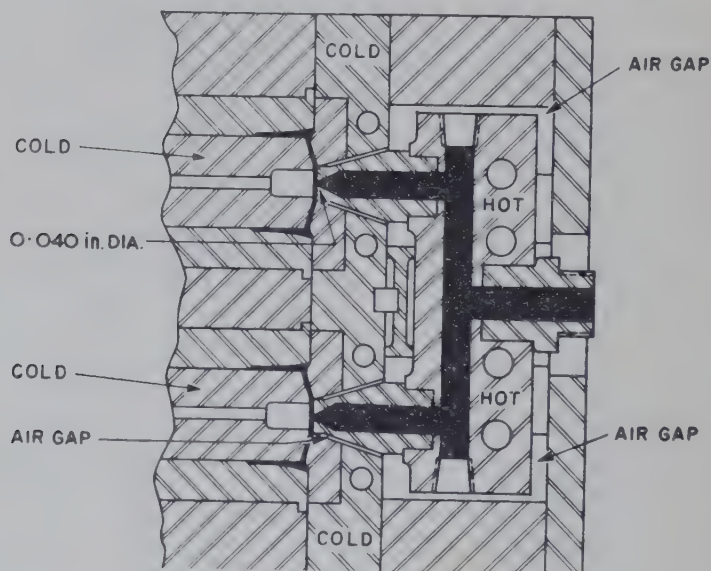


Fig. 19.7. Hot runner mould

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required to assure stripping the flexible sprue from the sprue bushing. The ejection of the part and runner system also require particular consideration. Because of the high shrinkage and material flexibility, the use of conventional knock-out pins are often ruled out and stripper rings and plates or air ejector systems are required.

The flexibility of polythene, however, allows the stripping of undercuts. For this reason parts such as snap-on container lids with a perimeter undercut can be stripped successfully. Moulded-in threads are also being successfully pulled from the metal die. This is exceptional, however, and only pertains to short, shallow threads. A more con-

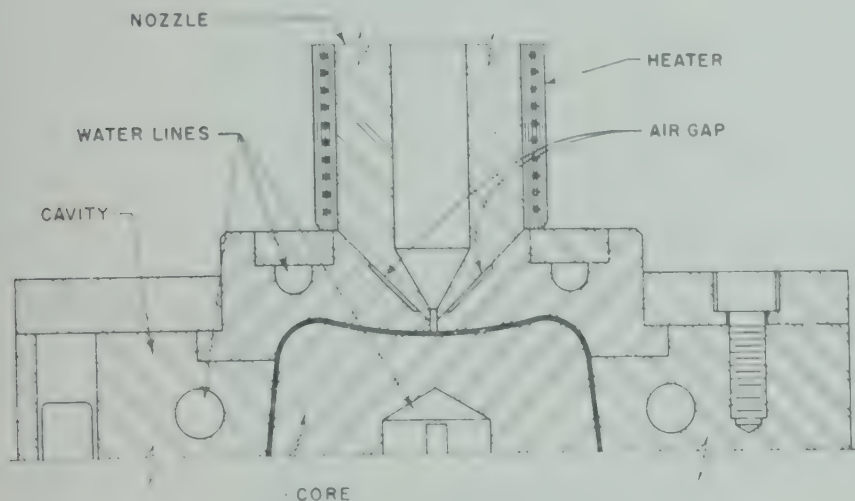


Fig. 19.8. Runnerless mould

ventional device such as an automatic core unscrewing design is usually used. Metal inserts can also be moulded into polythene.

Polythene lends itself readily to the successful use of hot runner moulds. The regulation of temperature to provide fluid material on one side of a gate and solid on the other side, only a fraction of an inch apart, is a difficult task with most moulding materials. Higher viscosity under moulding temperatures and a sharp freezing point contribute to the success of polythene in hot runner moulding.

The proper venting of moulds is important when moulding polythene because of polythene's tendency to oxidize and burn. In an insufficiently vented cavity, the air is trapped by the advancing front and compressed. The compressed air in turn causes high heats and burning of the material. Vents at the mould parting line should be about 0.002 inches deep and 1/8 in. to 3/16 in. wide for a length of about 1/2 in. and deepened to about 0.015 in. in a channel to the atmosphere.

The control of mould temperature is important to the successful moulding of polythene. The ease of moulding, surface finish and physical properties of the moulded part are all partly dependent on the right mould temperature. Adequate temperature control means that the entire surface of the mould cavity must be maintained at the proper

temperature. For best results on critical applications, temperature variation should not vary more than 5° – 10° F (3° – 6° C) across the mould cavity from the established mould temperature.

In practice the best mould temperature for polythene is usually 70° – 110° F (21° – 43° C). Higher mould temperatures cause some improvement in surface appearance but lower physical properties and increase shrinkage.

To assure good ejection of the part it is often desirable to cool one half of the mould to hold the part on the ejection side. In most cases, however, it is necessary to avoid widely different temperatures in the two mould halves to reduce high cooling strains and resultant warpage in the part. For adequate mould temperature control provision should be made for the movement of a large volume of heat exchange fluid with a minimum temperature differential between incoming and outgoing fluid. To obtain uniform temperature of the mould surface, channels should be placed in the cavity block and not in the plate behind it. Sometimes the cavity block must be made large enough to accommodate the channels and the ejector mechanism arranged so that adequate, properly located channels are obtained. In some cases, this will mean the use of special, rather than standard, mould bases; but they may be very well justified. All too often the channels are included more or less as an afterthought and prove entirely inadequate.

The heat exchange channels should be large, at least $9/16$ in. to $11/16$ in. in diameter. This provides a large area for heat transfer and prevents throttling of flow or stoppage of channels by corrosion.

DESIGNING POLYTHENE MOULDINGS

In the design of a new item to be moulded from polythene, the primary considerations are physical strength requirements and appearance. The effect of the product design on the moulding operation is of equal or even greater importance from the cost standpoint. Although the effect of variations in flow within the mould cavity is not as critical as for general-purpose polystyrene or acrylics, a small variation in section thickness, insignificant from the standpoint of strength or material costs, can make a part a very difficult, or a very easy, one to mould. Air traps, weld lines, and sinks can be controlled to a great extent by proper arrangement of flow within the cavity.

The most important rule in part design is to keep the wall thickness as uniform as possible. If one section of the cavity is thinner than an adjacent section, resistance to flow of the viscous molten polythene is greater in the thinner section. The increased resistance to flow reduces the velocity in the thin area which allows more rapid chilling of the material, further increasing the resistance and decreasing the velocity. It is entirely possible that even a small variation in section thickness can cause flow to cease completely in one area while allowing it to continue in an adjacent area. Often air traps or weak welds occur because of the manner in which this condition affects the flow within the cavity.

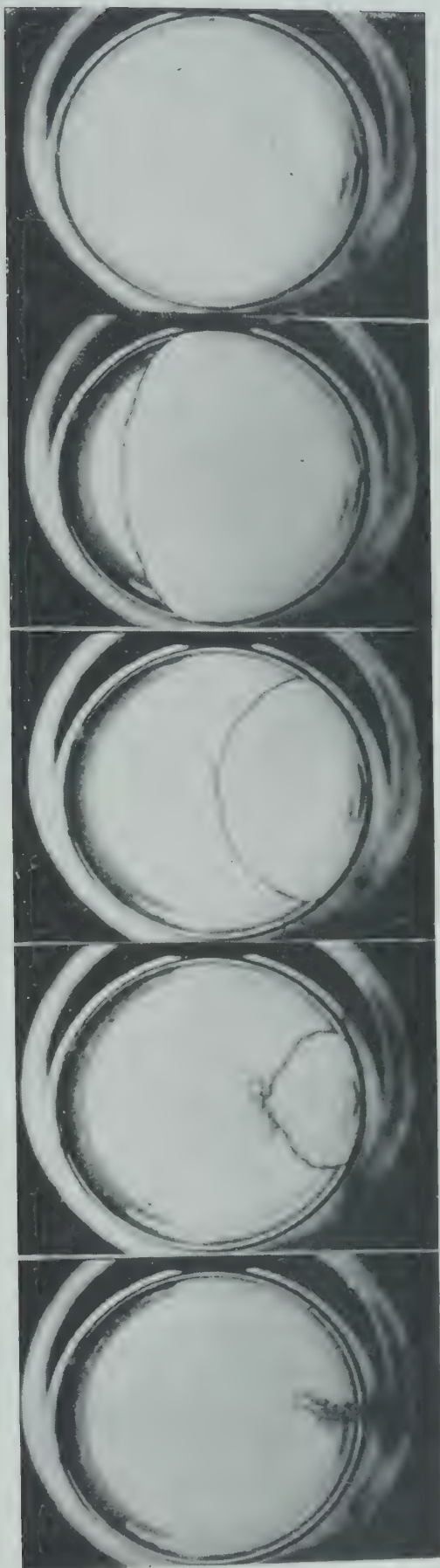


Plate 10. 1. Filling the mould cavity⁵ with polythene melt flow index 2

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Avoiding the use of heavy sections, heavy ribs, bosses and large fillets consists in the control of sinks which are caused by material shrinkage at the surface of large cross sections. Sometimes these bad features become a part of the product design for various reasons, and it may be necessary to work around them by means of flow control schemes. Increasing the section thickness slightly at the proper places as the material moves away from the gate may be helpful, and usually this is more effective than gate and runner alterations.

Reinforcing ribs and heavy sections of proper design can be used advantageously to stiffen a part. Because of the flexibility and high elongation of polythene, the ribs can be used where the mechanical loads are in tension. Usually the strength of the piece is more effectively increased by spreading the rib material uniformly over the area of the section. Ribs constitute a variation in section thickness and therefore may complicate the flow pattern unreasonably. Also, residual moulding stresses may be caused by the unequal cooling rate in the varying section thicknesses, and sink marks opposite the ribs are likely to occur.

If ribs do become necessary, it is recommended that their height be held to a minimum. The rib thickness should be approximately 0.010 in. thinner than the section to which it is attached, and the radius at the point of attachment should be in the range of 0.005 in. to 0.010 in.

Sticking of parts in the mould is sometimes a problem. Unnecessary undercuts in machining the die should be avoided. Mould surfaces may be etched or sand-blasted to overcome sticking, if necessary.

One of the predominant causes of sticking on multiple cavity shots is unbalanced gating. As a result of this condition, there is a considerable variation in the amount of pressure transmitted into the individual cavities. Therefore, excessive pressure may be transmitted to some cavities while others are barely filled. As a result, sticking occurs if the piece is difficult to eject. Proper gate balance avoids the trouble.

PROPERTIES OF MOULDINGS

Typical properties of injection moulded low density polythene of melt flow index 2 are shown in Table 19.3.

Table 19.3. PROPERTIES OF INJECTION MOULDED LOW DENSITY POLYTHENE

Melt flow index	2.07
Melt viscosity, poises, 350°F (177°C)	
(zero shear)	25,000
(700,000 dynes/sq.cm.)	10,000
Apparent density of granules, gm./ml.	0.47
Density, gm./ml.	0.92
Tensile strength, lb./sq. in. ^a	2810
Elongation, % ^a	53
Shore D hardness	46
Dissipation factor, 10 ⁶ cps	0.0001
Dielectric constant, 10 ⁶ cps	2.35

^a Dependent on moulding conditions.

POLYTHENE

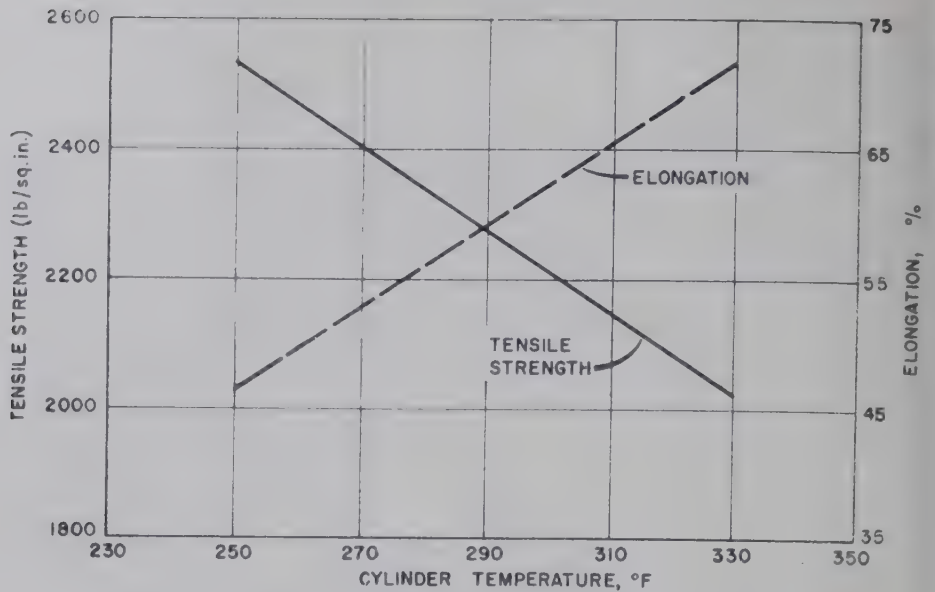


Fig. 19.9. Effect of cylinder temperature on tensile strength

The physical properties are affected by the moulding conditions, and it has been found that:

Increasing the cylinder temperature lowers tensile strength and increases elongation.

Increasing the polymer pressure lowers tensile strength and elongation.

Increasing the mould temperature lowers tensile strength and elongation.

These effects are illustrated in Figs. 19.9, 19.10 and 19.11. In general, the change of properties within the normal moulding range does not constitute a design problem. The strength is sufficiently great to suffice for most applications.

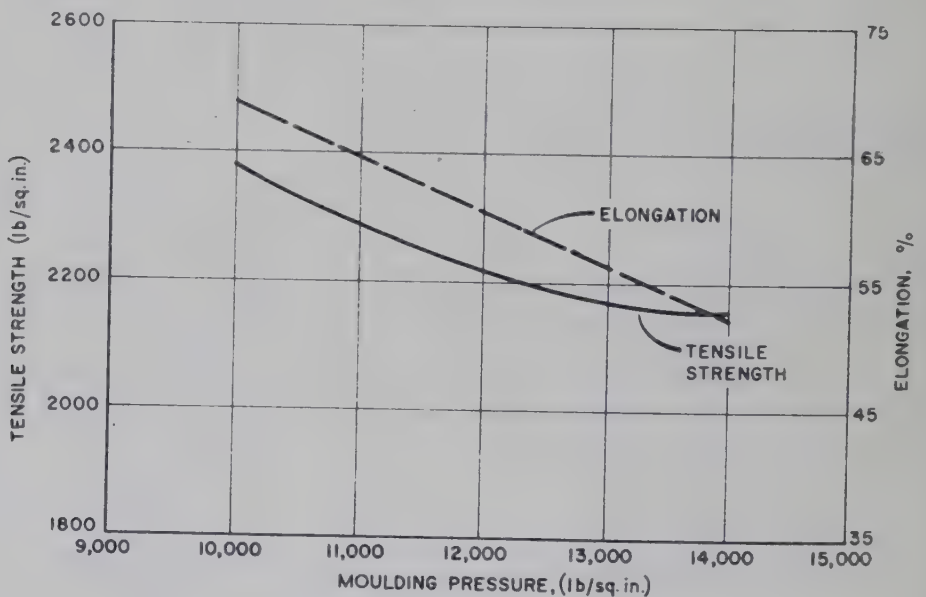


Fig. 19.10. Effect of moulding pressure on tensile strength

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Polythene mouldings exhibit the effects of orientation, but orientation or lack of it does not usually limit the usefulness of the material. For optimum properties, parts should be moulded as stress-free as possible.

It appears the chemical resistance and electrical properties of polythene are not influenced by moulding conditions. The chemical resistance of polythene is excellent, and so are the electrical properties, as discussed elsewhere.*

Little data are available on the effect of moulding conditions on environmental crack resistance. It seems reasonable that parts moulded

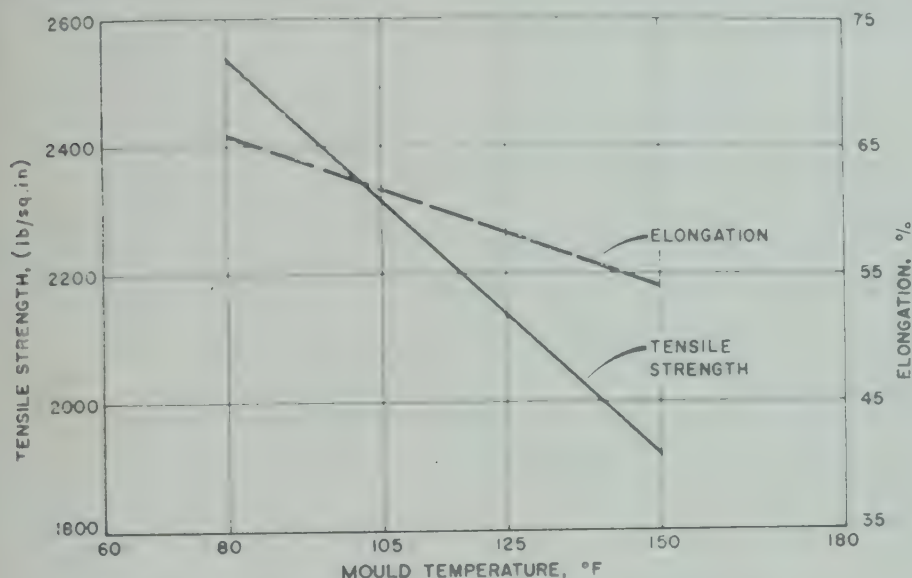


Fig. 19.11. Effect of mould temperature on tensile strength

under conditions where the polymer did not weld properly, particularly in the gate area, would be more susceptible to stress cracking than those moulded under optimum conditions. In any case, the effect of polymer molecular weight on stress cracking resistance appears to be much greater than the effect of varied moulding conditions.

MACHINING POLYTHENE

Polythene can be machined easily by standard machining methods. As formulations of polythene differ in flexibility and stiffness, machining speeds and techniques must be adjusted to suit the physical characteristics of the material used.

Tools should be made of high speed tool steel and kept well sharpened. All tools should have a shaving rather than a gouging edge. This tends to give a smoother finished surface that can be obtained when cutting tools with deep edges are used. High speed with proper tools assists easy cutting.

Feed pressure should be relaxed frequently enough to avoid overheating. If speed is required, water, preferably, or water-soluble oils

* See Chapters 10 and 8 respectively.

may be used as a lubricant. Devices for holding the material during machining should be cushioned to prevent marring or scratching surface. When it is found necessary to sand polythene, use of a very fine sandpaper will give a smooth surface which can be polished. High surface temperatures should be avoided since polythene will bind the tool.

When machining it is advisable to take relatively fine cuts when approaching the finished machine dimension desired and in cases where extreme precision is required to allow the rough cut machined piece twenty-four hours before final machining with fine cuts to the finished desired dimension.⁸

ADHESIVES AND SURFACE COATINGS

Because of its chemical inertness, solvent type adhesives cannot be used satisfactorily with polythene. Rubber base adhesives have been used in some instances. For best adhesion, the surface of the moulding should be treated. This can be done in several ways, i.e., treatment with hot air, flame, chlorination, or sulphuric acid-dichromate solution. The hot air or flame treatments are most prevalent.

Polythene is normally not surface coated. If destaticization is required, wetting agents or soaps will give temporary relief. Some wetting agents may be tumbled into the powder before moulding. Their effect is semi-permanent since they bloom with time to the surface of the moulding.

Some work has been done coating polythene containers with saran to improve barrier properties. Results are promising.

LINEAR OR HIGH DENSITY POLYTHENE

Recently a new type of polythene has been announced, and has received much publicity as an outstanding addition to the family of thermoplastics. It is produced by significantly different process techniques. Different names have been used to describe the material—"linear" is the authors' preference,* since the polymer essentially contains no molecular branching as does low density polythene.

Typical properties of a linear polythene compared to branched polythene (the product of the high pressure process) are shown in Table 19.4.

Linear polythene possesses the following advantages over branched polythene: increased rigidity (high modulus); increased temperature resistance; improved chemical resistance; better moisture and gas barrier characteristics; improved surface gloss on moulded parts.

At present, commercial moulding experience of linear polythene has been limited. In general, the same considerations discussed for branched polythene apply. But certain marked differences have been evident.

* Elsewhere in this volume we have used the term "high density" and "low density" for linear and branched polymers respectively.—*Editors*.

Table 19.4. TYPICAL PROPERTIES OF LINEAR POLYTHENE

Property	Linear Polythene	Branched Polythene
Melt flow index	1·18	2
Tensile strength, lb/sq.in. ^a	1600	1750
Yield strength, lb/sq.in. ^a	3500	1300
Modulus in tension, lb/sq.in. ^a	90,000	12,000
Elongation, % ^a	127	600
Density, gms./ml.	0·955	0·92
Vicat softening temp.	252°F (122°C)	205°F (96°C)
Low temp. brittleness,	< -75°C	< -75°C
Power factor, 10 ⁶ cps.	0·0001	0·0001
Dielectric constant, 10 ⁶ cps.	2·3	2·3

^a Compression moulded specimens.

Crystallinity is also a dominant factor in moulding linear polythene. This material is from 75 % and upwards in crystalline form, while branched polythene is about 60 %. Because of this, the density of linear polythene is higher—the molecules are packed more closely together.

Linear polythene also has an extremely short crystallization induction time. The crystallization begins at higher temperatures than branched polythene. Conversely, higher temperatures are required to melt the crystallites.

Viscosity data on linear polythene indicate the material is more shear sensitive than branched polythene, but much less than polystyrene. Table 19·5 gives data, at recommended moulding temperatures, which illustrate this point.⁴

The drop in viscosity of linear polythene due to moulding pressure is much less than polystyrene, but more than branched polythene. This also indicates that at actual moulding temperatures and pressures linear polythene is considerably more fluid than branched polythene.

In cooling, both linear and branched polythene stay relatively fluid and then abruptly harden as a certain temperature is reached. This temperature is higher for linear polythene than in the case of branched

Table 19.5. MELT VISCOSITIES OF POLYSTYRENE AND POLYTHENES

	Melt viscosity (poises) at moulding temp. given	Melt viscosity (poises) at moulding temp. given and pressure of 700,000 dynes/cm ²
Polystyrene (general-purpose)	24,000/450°F (232°C)	1,500/450°F (232°C)
Branched polythene (melt flow index 2)	9,500/450°F (232°C)	5,300/450°F (232°C)
Linear polythene (melt flow index 0·6)	5,000/500°F (260°C)	1,700/500°F (260°C)

POLYTHENE

Table 19.6. EFFECT OF MOULDING CONDITIONS ON TENSILE PROPERTIES OF A LINEAR POLYTHENE

Cylinder temp.	350°F 177°C	450°F 232°C	500°F 260°C	550°F 288°C	600°F 316°C
Tensile strength, lb/sq.in.	6,600	4,500	3,200	2,750	2,300
Yield strength, lb/sq.in.	No yield	No yield	3,700	3,450	2,850
Elongation, %	8	13	27	65	370

polythene. During the cooling in the mould, recrystallization takes place. This crystallization characteristic of these materials has an additional effect on moulding problems for the greater the extent of crystallization, the larger the shrinkage as the moulding cools and crystallization begins.

This means that dimensional control of linear polythene is more complex than with branched polythene. With linear polythene, which is more crystalline, the rate of crystallization is faster and crystallization begins at higher temperatures. Thus, the shrinkage is very large since it is due both to increased crystallization and thermal contraction over a wider temperature range. For this reason the problems of dimensional control on linear polythene may be far more involved than with branched polythene.

No data are yet published on the effect of moulding conditions on shrinkage for linear polythene. Data have been obtained however, on the effect of moulding conditions on physical properties (Table 19.6).

The elongation increases while tensile strength drops as cylinder temperature increases. Physically, the specimens moulded at low temperature exhibit "snap-brittleness"—sharp flexure will break them. Specimens moulded at higher temperatures can be flexed without breaking.

Linear polythene sets up faster in the mould since viscosity increases faster than branched polythene during cooling, and recrystallization begins at a higher temperature. But, to prevent extensive warpage, it may be necessary to use longer moulding cycles to insure that all shrinkage takes place in the mould where the part is restrained.

Typical properties of an injection moulded linear polythene are given in Table 19.7.

Table 19.7. TYPICAL PROPERTIES OF INJECTION MOULDED LINEAR POLYTHENE

Tensile strength, lb/sq. in.	2,560
Yield strength, lb/sq. in.	3,520
Elongation, %	50
Tensile modulus, lb/sq. in.	117,000
Impact strength (ft. lb/in. of notch)	2.4

The tensile properties appear very dependent on the rate of testing; with branched polythene the effect of rate of testing is slight.

INJECTION MOULDING

The chemical resistance of linear polythene is improved over branched polythene, as are the gas and moisture barrier properties. These improvements result from the increased density of linear polythene. The electrical properties of linear and branched polythene appear equivalent—both are excellent.

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CENTRIFUGAL CASTING OF LARGE DIAMETER PIPE

J. D. D. MORGAN

THE centrifugal casting process has been used for about 10 years for the manufacture of polythene pipes and has proved of great value for producing pipes of larger diameters than can be obtained conveniently by extrusion. In fact, centrifugally cast pipes up to 36 in. diameter and 12 ft in length are being produced successfully.

The process consists essentially of charging cold solid granulated polythene into a horizontal cylindrical metal mould which is heated externally and rotated on its longitudinal axis. When heated above its melting point, the polythene forms a viscous fluid which, under the centrifugal force, conforms to the mould wall. On subsequent cooling of the mould, which is kept rotating, the polythene solidifies as a pipe of uniform wall thickness which contracts from the metal mould wall due to its relatively high coefficient of thermal contraction.

EQUIPMENT

Two types of machine have been used; in one the horizontal mould is driven directly by the motor and in the other the mould rests on motor driven rollers. As the diameters and lengths of the pipes produced have increased, the roller driven machine has been found to be the more convenient and typical equipment is illustrated in Fig. 20.1 and Plate 20.1.

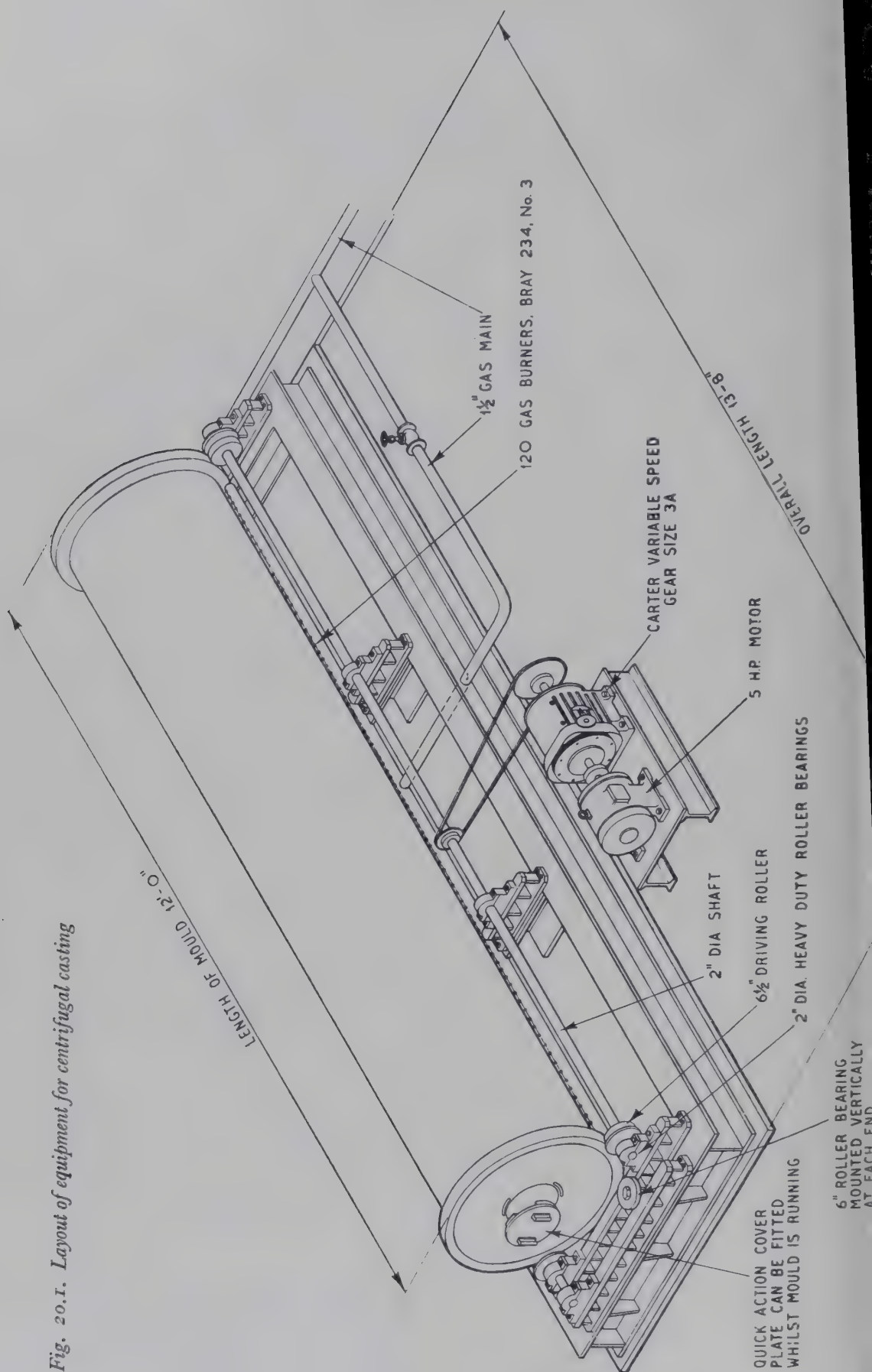
The machine consists essentially of: the mould itself; the gas burning system for heating the mould; the framework with rollers and shafts mounted on heavy duty roller bearings; and the motor drive with variable speed gear.

THE MOULD

The mould consists of a cylinder with rigid end flanges which rest on the driving rollers. Mild steel, aluminium and brass are suitable materials of construction and, as the surface of the cast pipe is a replica of that of the mould, the finish of the latter must be consistent with that required on the pipe.

In designing a mould to produce a given size of pipe, allowance must, of course, be made for the differential contraction of cast pipe and metal mould that will occur on cooling to atmospheric temperature. This factor also accounts for an appreciable longitudinal contraction.

Fig. 20.1. Layout of equipment for centrifugal casting



CENTRIFUGAL CASTING

The largest application of large diameter centrifugally cast pipe has been in chemical plant and most of this material has been produced in mild steel moulds. These have been fabricated by rolling and welding $\frac{1}{4}$ -in. plate and this thickness has been found to be satisfactory for moulds up to 3 ft diameter and 12 ft in length.

The moulds must be circular to ensure smooth running on the rollers and uniformity in wall thickness of the cast polythene pipe. In addition, the internal butt welds in the plate must be ground flush and the surface at least descaled to obtain a satisfactory surface finish.

It is common practice to dress the mould surface with soft soap or Lissapol C to prevent adhesion of the polythene and allow easy removal of the finished product.

HEATING ARRANGEMENTS

The mould should be heated to and maintained at a temperature of approximately 160°C while the polythene granules are being melted. Care must be taken to obtain even heating and also avoid overheating. At temperatures exceeding 180°C , there is a serious risk of oxidation of the polythene which would reduce the mechanical strength.

Gas burners are normally used for heating, a typical arrangement being that illustrated in Fig. 20.1. The heavy end flanges on the mould can lead to uneven and inadequate heating of the polythene and it is customary to apply local heat at these points by means of gas burners playing on the ends of the tyres.

GRADE OF POLYTHENE

Most of the early work on the centrifugal casting of polythene was done with melt flow index 20 material containing no anti-oxidant. The process, however, involves prolonged heating of the polythene in contact with air and the compound should, therefore, contain a suitable anti-oxidant. In addition, for pipes intended for external use or storage out of doors for long periods, it is essential that the polythene be protected from the effect of ultra-violet light by the incorporation of at least 2% of finely divided channel carbon black which must be thoroughly dispersed.*

METHOD OF OPERATION

The amount of polythene calculated to give the required wall thickness is first weighed. As wastage is confined to very small quantities trimmed from each end of the finished pipe, it is obvious that the wall thickness can be controlled accurately.

For large bore pipes, the moulds are preheated to approximately 130°C while rotated slowly. The polythene is then fed by hand and distributed as evenly as possible along the length. Subsequent rotation of the mould will complete the process of distribution and produce a pipe of uniform wall thickness. After charging, the mould is heated to approximately

* See Chapter 6.

160°C and the speed of rotation increased. These conditions are maintained until the polythene is uniformly melted, the appearance of the charge during melting is illustrated in Plates 20.2 and 20.3. After melting is then stopped and the mould is allowed to cool while still rotating.

The speed of rotation does not appear to be critical and the maximum speed is normally limited by the need for smooth running of the machine. A combination of motor speed, variable speed gear and of driving pulley diameter capable of rotating moulds at peripheral speeds up to 100 ft/min is suitable for producing all sizes of pipe up to 3 ft diameter.

A typical operating cycle for producing pipe of 3 ft diameter and $\frac{3}{8}$ -in. wall thickness and 12-ft length is given in Table 20.1. It will be seen that a time cycle of 4–6 hours is required for large diameter pipe, the actual time depending on the melt flow index of polythene used.

QUALITY OF PRODUCT

The mechanical properties of cast pipe are generally inferior to those of extruded pipe but the harder grades of polythene containing antioxidant and carbon black give cast pipe with mechanical properties closely approaching those of extruded pipe. It has also been found that when using polythene containing anti-oxidant and carbon black the surface appearance of the pipe bore is much better than that of pipe made from material without additives. The latter gives pipe with a granular surface appearance at the bore and the improvement with additives is illustrated in Plates 20.4 and 20.5.

TYPICAL APPLICATIONS OF CENTRIFUGALLY CAST PIPE

Most of the centrifugally cast polythene pipe so far produced has been used for chemical plant and effluent drains where chemical resistance, lightness and ease of fabrication and erection have shown to advantage. There are, however, complex engineering problems associated with the use of such a material with its low mechanical strength and high coefficient of expansion as compared with conventional materials of construction. When allowance is made for these limitations, the advantages listed above are very attractive and typical applications are illustrated in Plates 20.6 and 20.7.

Table 20.1. TYPICAL TIME CYCLE FOR CASTING PIPE

Operation	Melt flow index 20	Melt flow index 2
1. Start rotating mould at 10–15 rev/min		
2. Heat mould from cold to 130°C	45 minutes	45 minutes
3. Load mould (200 lb polythene)	30 minutes	75 minutes
4. Increase temperature to 160°C and speed to 40 rev/min	25 minutes	40 minutes
5. Maintain these conditions for		
6. Cool to 40°C	20 minutes 2 hours	80 minutes 2 hours



Plate 20.1. Centrifugal casting machine with cast pipe 11 ft 9 in. long and 36 in. diameter

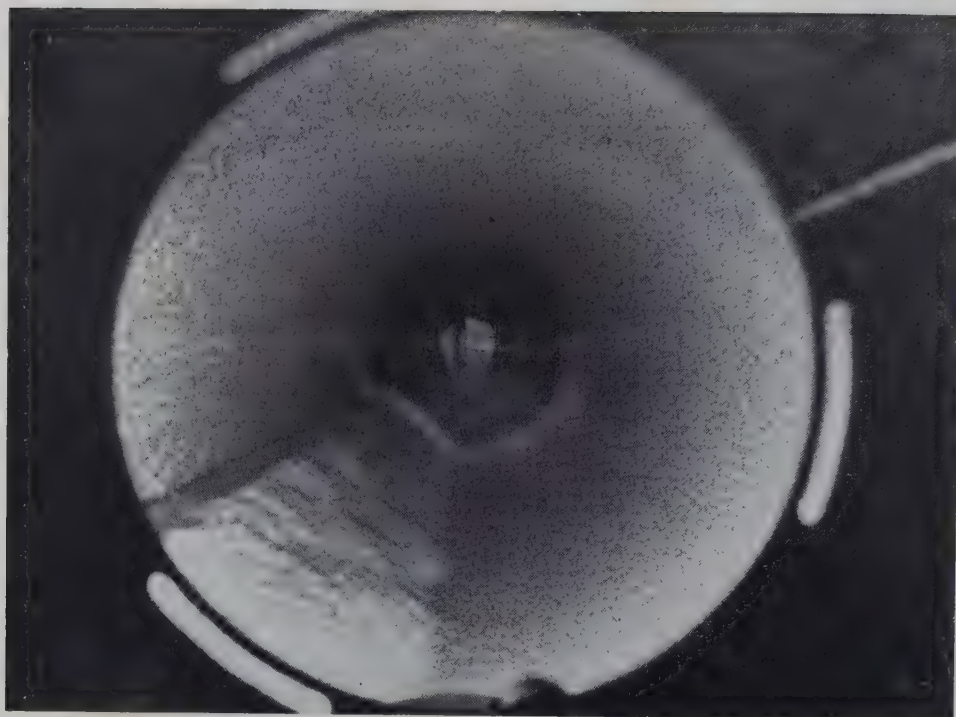
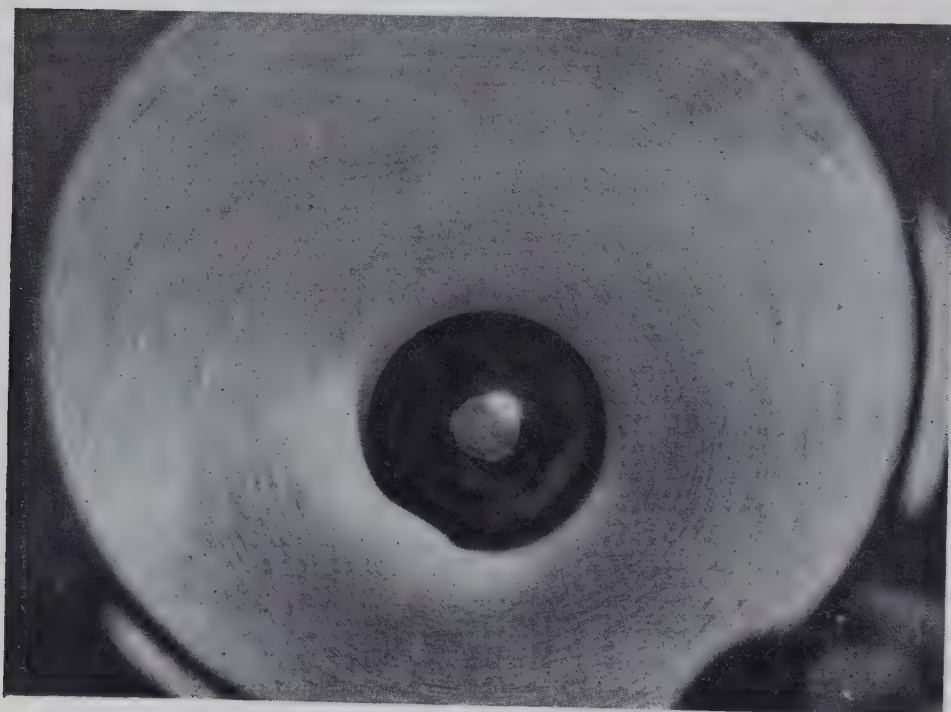


Plate 20.2. Interior of mould shortly after loading with polythene. Unpigmented polythene was used to give good photographic reproduction

Plate 20.3. Interior of mould early in spinning period. Unpigmented polythene was used to give good photographic reproduction



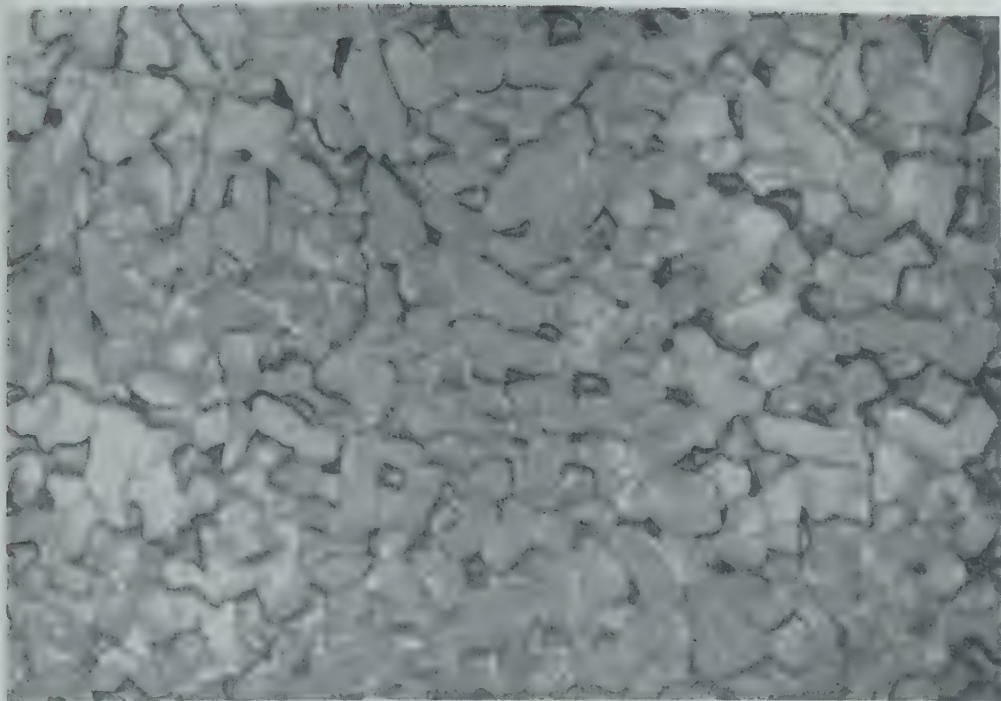


Plate 20.4. Granular surface appearance at bore of centrifugally cast pipe made from polythene containing no additives

Plate 20.5. Surface appearance at bore of centrifugally cast pipe made from polythene containing anti-oxidant and carbon black



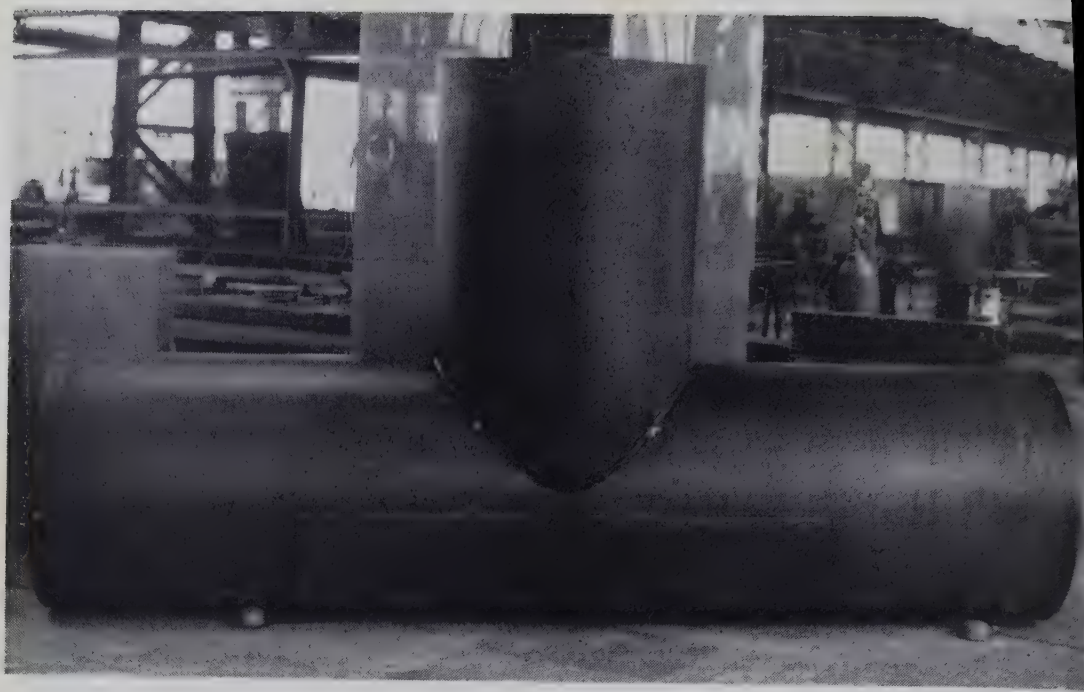
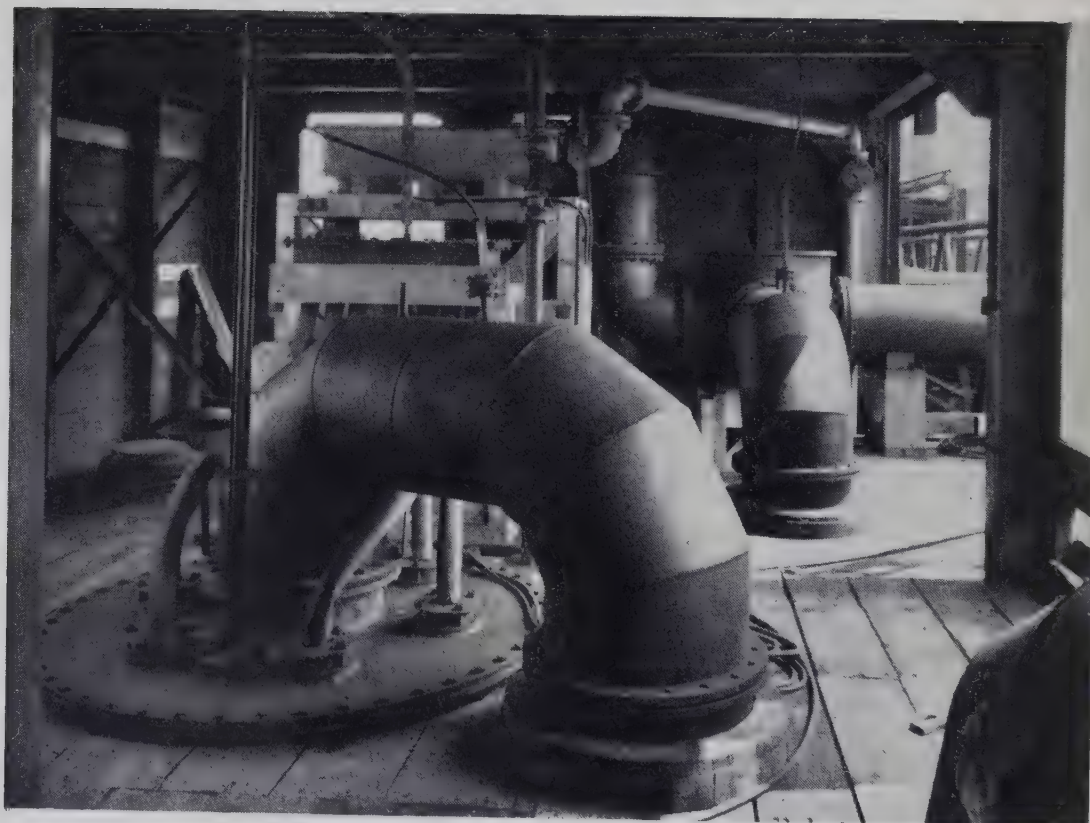


Plate 20.6. Welded tee-piece of 36 in. diameter pipe for drain manhole

Plate 20.7. Fabricated 18 in. diameter pipework



PAPER COATING

W. H. WILLERT

THIS chapter is devoted entirely to the subject of surface coating of various flexible surfaces with polythene, describing in detail the "extrusion coating" or "laminating" method which is the most universally used process. In order to appreciate the process better its background and development will be described first.

After World War II new uses for polythene were sought and development activities were directed to the packaging field where a large potential market awaited a material such as polythene which was light, flexible (even at low temperatures), odourless, non-toxic, chemically resistant, inexpensive, and above all had a very low moisture permeability. In a few years a technique to produce unsupported polythene films was developed which has been described in Chapter 18.

At the same time the paper industry was looking for a cheap coating material which produced a moisture and chemical resistant packaging material. Polythene had the desired properties. Samples made in the laboratory produced a dimensionally stable, flexible, and strong packaging material thus extending the market for paper and plastics into new fields. It remained to develop a fast, economical method for applying or laminating the polythene to the surface of the paper or other base materials.

METHODS OF PAPER COATING

Naturally the development of a suitable method of applying polythene to a paper web proceeded along the lines of known arts using equipment which was already available in the converting departments of the paper mills. Some of the common methods will be discussed briefly, indicating the modifications which were made, the advantages over other methods, and the disadvantages or limitations of each process. As there is at present no commercial experience of coating paper with the new high density polythene all the methods discussed will refer solely to the low density polythene.

Solution coating

In one of the first methods tried, polythene was dissolved in a solvent and applied to the web by a well known procedure using standard pieces of coating equipment such as the roll coater (Fig. 21.1) or the reverse roll coater (Fig. 21.2). (See Chapter 12).

With the roll coater the coating may be applied directly from a roll revolving in a pan of the coating liquid, in this case a solution of polythene;

another arrangement of the roll coater shows the use of a transverse. Using precision ground chilled iron rolls very accurate coating weight can be applied. Subject to any variation in the web thickness roll coaters have a number of disadvantages which are overcome by the reverse principles, the thickness of the coating on the casting roll being controlled by the metering or doctor roll travelling in the opposite direction. The final thickness of coating is independent of web thickness. One of

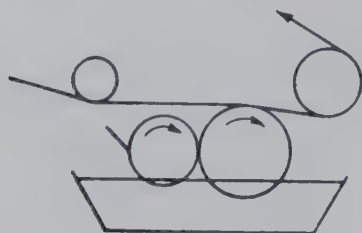


Fig. 21.1. Roll coater

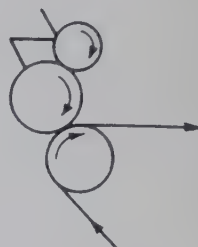


Fig. 21.2. Reverse roll coater

limitations is that the coating is usually limited to a minimum of about 0.001 in. measured in the wet thickness.

A difficulty with both these methods was the inability to obtain a suitable solution of polythene, which is practically insoluble in all organic solvents at temperatures below 50°C. A good solvent is xylene and the concentration of a polymer of melt flow index 2 is limited to approximately 35% by weight at 100°C. Greater concentrations or lower temperatures result in gelation or insolubility when the low solvent content and the need for removing the solvents from the coating results in an inefficient and costly method. Solvent recovery systems can make the method more economical but other limitations are the explosive hazards and the difficulty of removing all the solvent from the web in order to obtain a

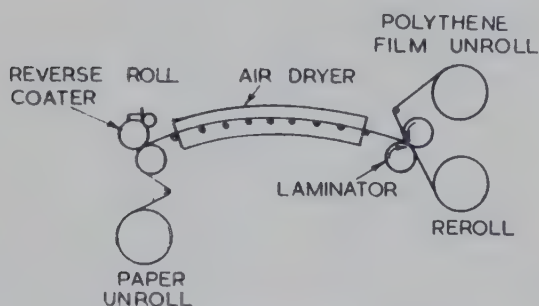


Fig. 21.3. Polythene film laminator

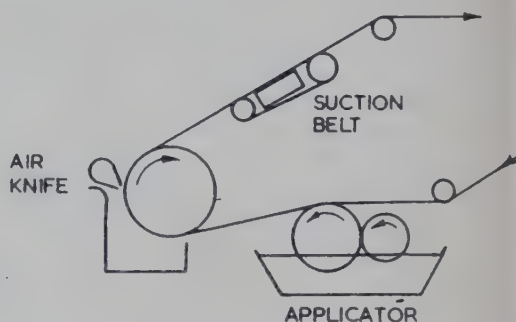


Fig. 21.4. Air coater

non-toxic packaging material. For these reasons this method was abandoned.

Combining unsupported film to paper with an adhesive

Unsupported polythene film is available in a range of thicknesses and it can be combined with paper by the use of suitable adhesives (Fig. 21.3). The pressure sensitive types are most commonly used; adhesives contain-

ing solvents are not too satisfactory as the volatiles have to be removed through the web and the adhesive does not attack or penetrate the surface of the polythene. This method is usually relatively expensive since it is carried out at relatively slow speeds and the coating is limited to the thickness of film which is available. This is usually 0.001 in. or thicker.

Emulsions

With the development of polythene emulsions, which are made by suspending finely divided particles of the polymer in aqueous solution, an air coater (Fig. 21.4) has been used with some success. In this method the emulsion is applied to the web with an applicator roll running in the pan containing the emulsion. The coating thickness is controlled by blowing the excess off the surface with air at a controlled velocity, direction, and pressure. The water is removed and the polythene fused to the web by running it through a suitable drying oven. The cost of the emulsion and the subsequent drying and fusing operation is relatively expensive and consequently the use of this method has not been widespread.

Knife coating with a hot melt

One logical approach to the problem was to apply the polythene to the web with a knife coater (Fig. 21.5A). The main difficulty of this method was to produce a suitable hot melt. Polythene is a very poor conductor of heat and it is difficult to obtain a uniform and thoroughly

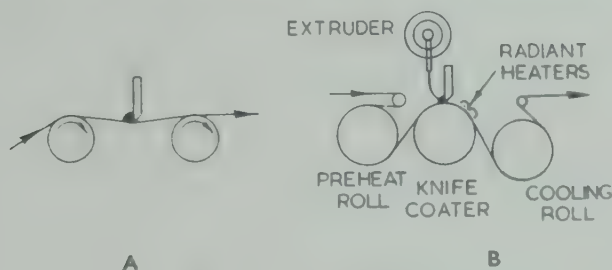


Fig. 21.5. Knife coater

melted bank of polymer ahead of the knife. This difficulty was overcome by using an extruder (Fig. 21.5B). However, two difficulties remained; firstly polythene at elevated temperatures is subject to oxidation when in contact with air, and secondly a uniform coating thickness is dependent upon a uniform web. Since the high viscosity of the melt produces considerable drag another difficulty arose with breakages of the web. This method, however, usually produces a good bond and does not have the disadvantages of those methods where solvents or carriers have to be removed.

Extrusion coating

None of the existing techniques, although modified, produced a completely satisfactory and economical process for laminating polythene

to paper. A modified extrusion method of producing unsupported with acceptable thickness tolerance from a flat manifold type die been developed to a commercial process. The possibility of extruding hot film directly from the die on to a moving web was investigated

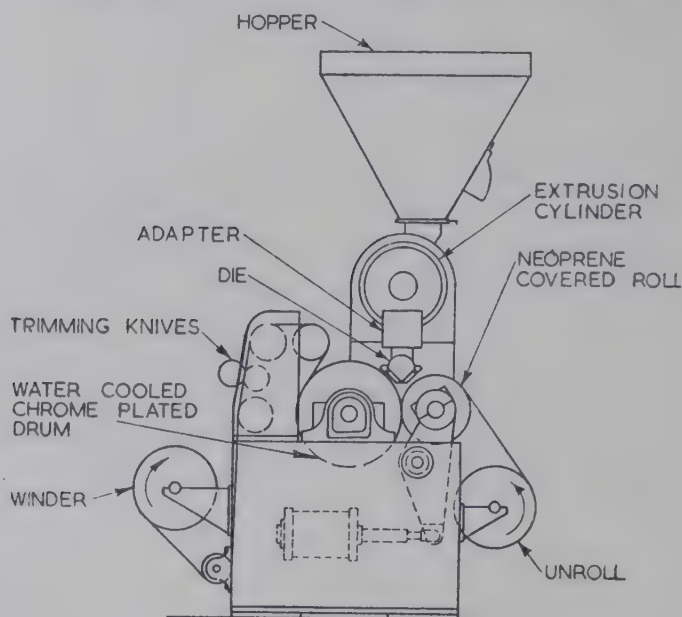


Fig. 21.6. Extrusion laminator

subsequent development has resulted in the "extrusion coating" process as it is known to-day.

This process (Fig. 21.6) is quite economical and the equipment required and its operation will be described in detail.

EXTRUSION COATING PROCESS

The polythene in granular form is placed in the extruder hopper. The screw conveys the polymer along the extruder barrel where it is heated to a predetermined uniform temperature and consistency. Automatic temperature controllers regulate resistance type heater bands on the barrel, thus controlling the final melt temperature of the polythene. The extrusion rate is controlled by regulating the speed of rotation of the extruder screw. The polythene passes through a screen filter on the breaker plate and through an adaptor connecting the extruder barrel to the die.

The die known as a sheeting, film, or laminating die, is also heated and its temperature controlled by a number of automatic units. Each controls individual sections along the length of the die. A number of adjusting screws are used to control the opening of the die lips and consequently the thickness and uniformity of the film as it emerges from the die.

The laminating section consists of a specially constructed chromium plated cooling drum against which rides a rubber or neoprene covered

pressure roll. The pressure between the two is carefully controlled by air cylinders. Whether it be paper, cloth, or foil, the web comes from the unwind stand over the rubber roll and around the cooling drum to the winder. At the nip of the laminating rolls the hot polythene sheet is applied to the web. Here the adhesion or lamination is produced. As it runs around the cooling drum the polythene is cooled sufficiently to come free of the drum surface before passing to the winder. Since a bead occurs at the edges of the sheet the web is trimmed to width before it is wound up into a roll.

Once the operation has started it will run continuously, the thickness of the coating being controlled by the web speed and the extrusion rate.

Before starting up the coating operation all precautions should be made to ensure that the various parts of the equipment are operating satisfactorily. Although no exact setting of the opening between the die lips has been proven theoretically it is known that a smaller opening is desirable for better distribution of the polythene, especially for wider coatings. However, wider openings are desirable for removing foreign material which may lodge behind the lips. Also with wider openings there is less error in the uniformity of the coating as the film is drawn down to approximately the same coating weight independent of the opening. In practice it has been found that this opening can be varied from 0.010 in. to 0.035 in. without much effect on the results. It is recommended that it be set to an opening between 0.015 in. and 0.020 in. using a feeler gauge to check that the opening is constant to within 0.001 in. over its entire length. Care should be exercised to ensure that both lips are level across the bottom. When the lips have been set they should be sprayed or covered with a silicone mould release compound.

It is advisable that a screen pack on a breaker plate be fitted in the barrel at the end of the screw. Although this helps to homogenize the polythene it is not necessary with a properly designed screw, but is required nevertheless to remove foreign material which might clog the die orifice. A screen pack of 80 mesh followed by 100, 120, 100 and another 80 has been found satisfactory for most compounds and operations. After operational experience the screen pack assembly may be altered for a specific purpose, for example, the rather heavy coating of polythene combined with Kraft paper used for liners in multiple wall bags. The thickness of the screen pack can be reduced or the screens made coarser by eliminating, say, the 100 and 120 mesh screens. On the other hand, if Cellophane is to be coated with a thin layer several screens of 150 mesh can be added.

The temperature along the extruder barrel on the adaptor and the die should be allowed to rise slowly until a temperature gradient has been attained which from experience is found to be suitable for starting. Water should be circulated through the feed section and screw during the warming up period in order to prevent these parts from becoming overheated. The extruder should be started at its lowest speed and polythene granules fed into the barrel, through the hopper. After

allowing time for the material to fill the extruder, adaptor, and die will commence to emerge at the lips. The film produced initially contains impurities which will clear up after about 15 min. Any material behind the die lips should be cleared with a small brass screwdriver.

It is essential that the output of the extruder, already determined by various screw speeds by calibration, should be accurately set according to the web speed and the thickness of coating required. Also the polythene sheet width should be regulated at this time to correspond to the web width. This is accomplished by pushing in the deckle rods an equal amount from each end. In passing, it should be appreciated that polythene having a specific gravity of 0.92 has a theoretical yield of approximately 208 sq. ft. or 30,000 sq. in. per pound for a 0.001 in. thick coating. In the standards of the paper industry this is approximately 14.7 lb. per ream based on 3,000 sq. ft. (in the metric system a 0.001 in. coating is equivalent to about 23 grams per square metre).

Another point to watch is that the polythene is distributed uniformly across the web. This can be accomplished in two ways. The first is to keep the die opening uniform and vary the temperature of the various zones along the die and so change the viscosity of the melt; the second, which is only used to control the gauge over short distances within the temperature control zone, is accomplished by moving the die lips in and out with either the push or pull screws. Higher temperatures result in lower melt viscosities producing heavier coatings and vice versa. The lower melt viscosities also reduce the pressure drop in the die, increasing the flow at these points.

After all these adjustments have been completed the extruder should be stopped, the paper threaded through the machine, and the die located in position over the nip between the two rolls. The web should then be started at its minimum speed, followed immediately by starting the extruder. To begin with, the rubber roll is in the open position and the polythene is extruded on to the web. After it has been threaded around the cooling drum the rubber roll can be moved up to close the nip. At this point one should check that the polythene sheet width corresponds to the position of the web. Having accomplished this, the extrusion rate and the web speed should be brought up to their predetermined values to give the proper coating weight. The deckles should be moved out so that the coating can be uniformly applied along the edge of the sheet. If the rubber roll has been cut back so that it corresponds with the web width the coating should be extended by approx. 1 in. beyond each side of the web. This excess is trimmed off and the tension of the web on either side of the machine adjusted before increasing the speed of the extruder and the web to obtain the maximum production rate. The coating thickness should be checked over the first few hours of operation and corrected as necessary.

If for any reason the web has to be stopped the extruder should be shut off immediately and the rubber roll moved away to open the nip. For periods of down time exceeding 3-4 min. it is advisable for the die and

extruder to be backed out of the coating position and the extruder started at a minimum speed to prevent the polythene from burning in the die. If this arrangement is not possible a catch pan is placed under the die and above the laminating rolls to catch the material. In all cases this down time should be kept to a minimum.

OPERATIONAL PROBLEMS

Poor adhesion

Poor adhesion or bonding of the coating to the web is usually due to low polythene temperatures; with the aid of a thermocouple located in the adaptor this can be readily determined. For polythene of melt flow index 2 this temperature should be about 315°C . If the temperature of the polythene melt drops below 305°C the bond will drop off sharply. This can be corrected by increasing the temperatures of the extruder barrel. As the rate of extrusion is increased the velocity of the polymer in the extruder is increased, resulting in lower final melt temperatures. In some cases settings as high as 400°C may be made, but care should be exercised in not getting the temperature too high, since pyrolysis of the polythene will then occur, resulting in chemical breakdown.

If higher temperatures do not improve adhesion, the next point to check is the relative positions of the nip between the rubber roll and the cooling drum, the die, and the point at which the polythene film strikes the web. If the polythene strikes the cooling drum first it will solidify and not stick to the web. If it should meet the web a sufficient distance ahead of the nip the web will cool it and cause spotty adhesion. The best condition is for the polythene to strike the web exactly at the nip and tangential to the rubber roll. The cooling drum can be adjusted horizontally and the rubber roll adjusted vertically to obtain the correct position.

Another cause of poor adhesion is insufficient laminating pressure. In most cases loads from 50–75 lb per linear inch at the nip are required. These can be controlled easily by changing the pressure of the air supplied to the cylinders which are attached to the pivot arms of the rubber roll.

The type of web has an important bearing on the adhesion achieved; for instance, an extremely coarse web such as hessian will only give adhesion at the high points. Moisture on the surface of the web will evaporate when the polythene touches it, causing bubbles and poor adhesion. Certain sizing or coatings on the web itself will interfere, as will lubricants on the surface of aluminium foil. It is essential that the surface should be clean of any oil or grease. Certain webs such as Cellophane require special anchor coatings in order to obtain suitable bonding. Where thin coatings are required, preheating of the web may be necessary.

The temperature of the chill roll is important too. A low temperature may cause the polythene to cool off too rapidly, especially the thin coatings. A high surface temperature may cause it to stick to the roll, thereby parting the coating from the web as it is stripped from the surface of the

roll. The condensation of low molecular weight polythene on the surface has a similar effect. For this reason the cooling drum should be kept clean by washing it periodically with toluene. Its temperature should be carefully controlled at all times; a higher temperature rather than a lower temperature is more likely to have an adverse effect.

Voids in the coating

Voids can be caused by moisture in the molten polythene, or by over heating. Sometimes moisture can be present in the raw material, or by condensation on cold granules which have been brought into a room where the humidity is high.

If the extruder is stopped for a few minutes at high operating temperatures the polythene will decompose, causing pockets of volatile hydrocarbons to form, resulting in bubbles; this is usually accompanied by slight discolouration of the film. Lowering the temperatures or running the extruder for a few minutes at a high output should eliminate this particular type of trouble.

Uneven coating

Uneven coatings or large voids can be caused by too low a melt temperature when the polythene is extruded; at extremely low temperatures it cannot be drawn down uniformly. Raising the melt temperature usually corrects this situation, although sometimes it can be traced to decomposition or foreign material coming from the extruder, causing momentary clogging at the die opening. This latter fault can be determined by observation. Uneven coating at the edges of the web is due to too low temperatures at the die extremities. As the polythene is drawn down to the coating thickness it will tear longitudinally rather than stretch. Again higher temperatures should correct the fault. There are occasions when leakage around the deckle rods causes feathering of the edges. It is then advisable to check the seating of these rods and if necessary replace them.

Leakage at the end caps

Leakage at the end caps around the point and where the deckle rods enter can be minimized by lowering the temperature on the ends of the die to about 205°C. If they are lowered beyond this point heat will be drained away from the rest of the die giving poor control. The temperatures on the ends should be lowered to a point where the polythene becomes sufficiently viscous not to exude from small openings.

Carbon in the coatings

Carbon is formed by decomposition or oxidation of the polymer. It can be prevented by running the extruder at slow speeds during production stoppages. If the product becomes unacceptable because of carbon, the die lips should be removed, polished, and coated with silicone grease before replacing.

Odour in coating

This is one of the most frequent problems encountered when producing packaging materials for foods and is caused by overheating the polymer. Sometimes this breakdown has occurred in the processing carried out on the compound before it is received.

The odour can be minimized by keeping the temperatures along the extruder barrel and in the die no more than 5–10°C above the actual melt temperature. For this reason it is sometimes necessary to extrude at low outputs where thin odourless coatings are being produced. It should be pointed out that after a prolonged shut down the extruder should be operated at the normal production rate for several minutes before attempting to coat. This will flush out of the extruder any polymer which may have been overheated.

Equipment

As already mentioned, the polythene is extruded at unusually high temperatures at which it readily oxidizes in the presence of air, causing discolouration and carbonization. When the extruder is stopped for any length of time the polythene will overheat and, due to its low viscosity, will drip from the die. This results in air entering the die where there is a large surface area of the polythene clinging to the hot metal. The resulting formation of carbon will contaminate the polythene when the extruder is restarted. The length of time stopped and the temperature of the die, determine the degree of oxidization which will have occurred. For this reason the coating operation should be planned with the minimum amount of interruptions and downtime. Thus it is obviously better to operate on three shifts each twenty-four hours than on day-work only.

However, where the recommended method cannot be worked certain procedure can be followed which will minimize the defects described above. Assuming that the extruder is operating at the proper temperature the following procedure is recommended for shutting down the unit:

- (i) Turn the power off all heating zones except that immediately in front of the hopper section on the extruder barrel. That should be turned down to 200°C.
- (ii) Continue to run the extruder at the same output until the melt temperature is such that poor adhesion commences. This is usually around 308°C and will occur from 5–10 min. after the heaters have been turned off.
- (iii) Reduce the output and the web speed maintaining the minimum melt temperature. Then continue to reduce these rates until approximately 25% of the machine's rated capacity is reached. On smaller machines this capacity may be set immediately after deciding to shut the unit down.
- (iv) After the temperatures have been reduced to the point where it is impossible to maintain the coating operation at the reduced extrusion rate, drop the screw speed to its minimum and continue

to extrude polythene through the die, catching it in some of container. If the installation includes a carriage this operation will be carried out with the die in the out-of-coating position.

- (v) When the die temperature has dropped below 205°C the operation can be stopped as the polythene will have reached a viscosity at which it will no longer drip out of the die. After the coating operation has been discontinued the use of air jets will help to reduce this temperature at a faster rate.

When starting the extruder up again the following procedure is recommended:

- (i) Set all the temperatures of the various zones at 205°C .
- (ii) Scrape the polythene from the die lips using a copper metal cleaning pad and coat the opening and area around it with a silicone mould release compound.
- (iii) Start the extruder at its lowest screw speed.
- (iv) Increase the temperature setting in the various zones to the previous running conditions until the melt temperature reaches the minimum at which the coating operation can be started.
- (v) Resume coating speeds as soon as conditions permit.

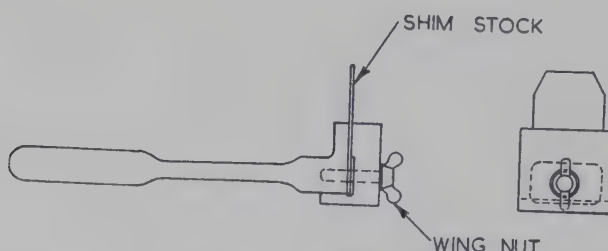


Fig. 21.7. Cleaning tool

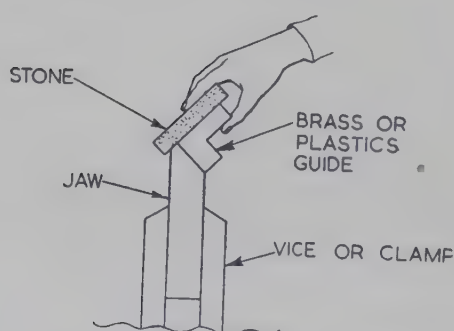


Fig. 21.8. Honing die jaws

It is difficult completely to avoid oxidization conditions. As previously described, when small particles of carbon lodge behind the die lips causing streaks in the coating, the coating operation should be stopped and the carbon particles removed with the aid of a brass tool (Fig. 21.7). The

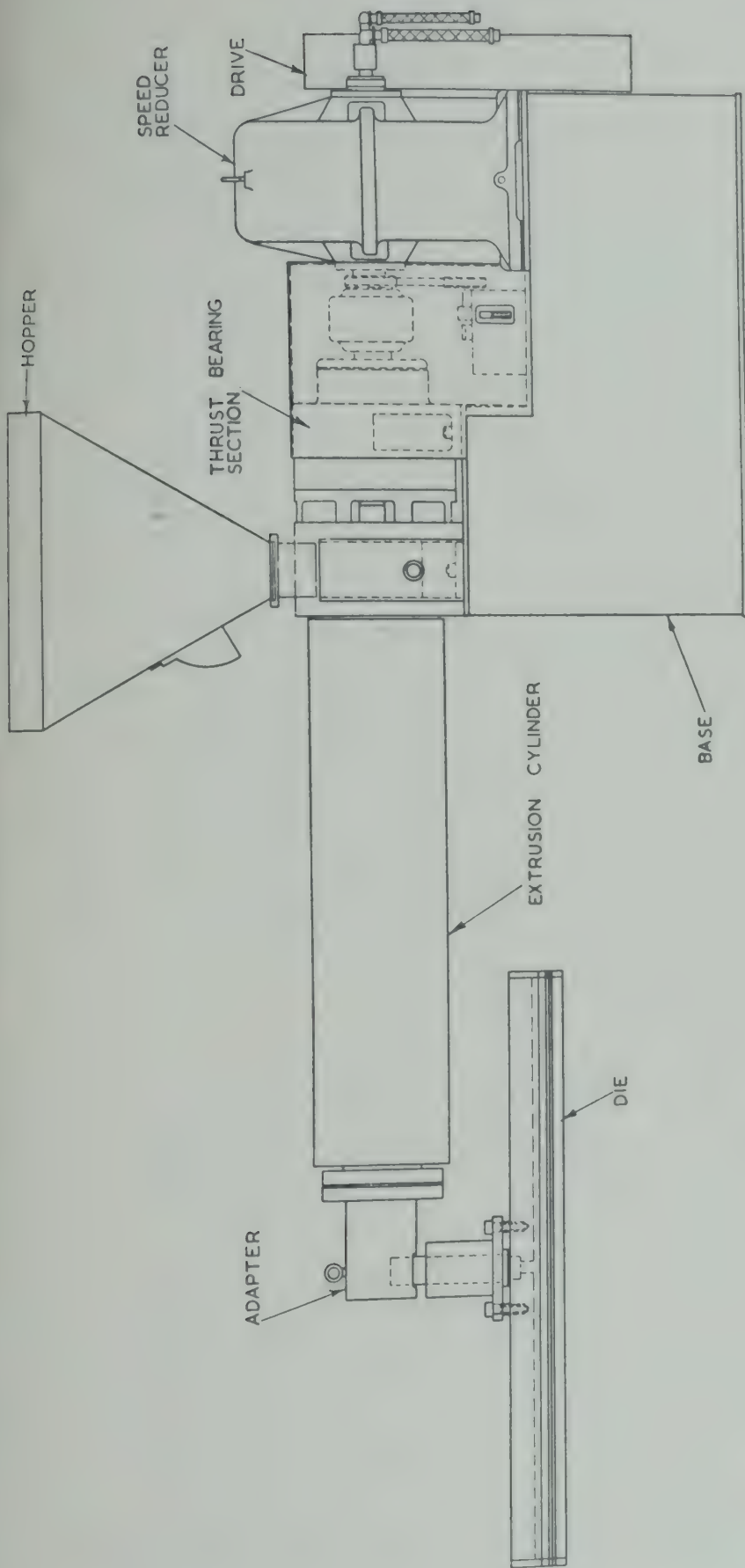


Fig. 21.9. Standard style of extruder for extrusion coating

coating of the tool with silicone grease will prevent the polythene sticking to it, making it easy to clean.

After the extruder has been started up and shut down approximately three to five times it may be necessary to clean the die lips. These should be removed and cleaned thoroughly with soft copper tools and Scotch pads until all the polythene and foreign materials have been removed. It may be necessary to polish the die lips using honing stones (Fig. 2). Then care must be taken to ensure that the sharp edges are not rounded off and that the surfaces remain smooth and true. Starting with relatively coarse honing stones of approximately 300 grit the surfaces are thoroughly cleaned down to the bare metal. The final honing should be done with stones in the neighbourhood of 500 grit. Long uniform strokes should be used to prevent nicks and blemishes on the surface.

Another maintenance job consists of changing the screen pack when it becomes clogged; the frequency of this change will depend upon the cleanliness of the particular operation and of the polythene. Screen changes may be necessary from once a day to once every six months. The need for changing the screens can be observed from a reduction in output or the need to increase screw speed and h.p., to maintain a specific extrusion rate. The screens should be changed when the extruder parts are between 180 and 200°C; if carried out at higher temperatures oxidization will occur resulting in immediate clogging of the screen again and contamination of the coating with carbon particles.

Other points which should be checked frequently, say each week, are the operation of all the heater bands, and the calibration of the thermocouples. Screw threads of parts connecting the die to the extruder should be lubricated, to prevent binding, with molybdenum or copper sulphide or a graphite and water paste. In all cases petroleum products should be avoided since they will carbonise at the high temperatures; silicones are equally ineffective.

DESIGN OF EQUIPMENT

It will be appreciated that in the design of the various components there are certain details which are significant to ensure the best performance. The components which make up the extrusion coating process are the extruder, adaptor, sheeting die, laminating section, unwind winder, motor drives and accessories.

Extruder. This is a standard electrically heated single screw extruder (Fig. 21.9) similar to the type already described. The hopper or feed section and the screw can be cooled with water. The screw has a uniform pitch with two flight depths which are constant over the first two-thirds and the last one third of the screw respectively. At the two-thirds point there is a rapid decrease in flight depth, the compression ratio being about 4 : 1. (See also Chapters 15, 17 and 18.)

Adaptor. The adaptor (Fig. 21.10) is connected to the extruder barrel by a clamp or swing bolts; this enables the operator to break the joint

PAPER COATING

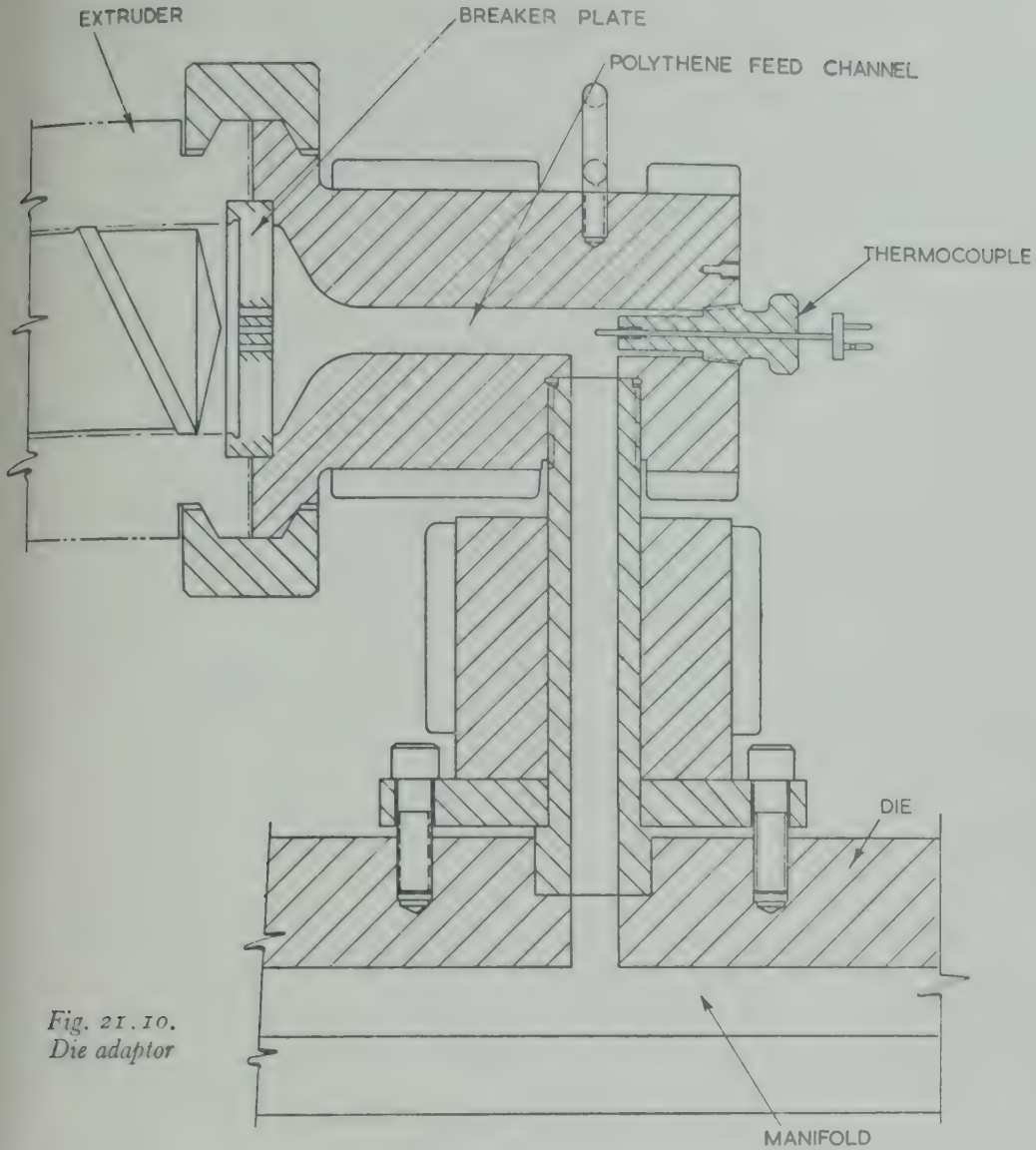


Fig. 21.10.
Die adaptor

quickly so that the breaker plate can be easily removed when screen changes are required.

The functions of the adaptor are to direct the flow of polythene from the barrel to the die, to support the weight of the die and maintain the latter's alignment with the nip of the laminating rolls. In addition, it should be compact, uniformly heated and easily taken apart for cleaning. The plug used to support the melt thermocouple also acts as a bleed point.

Sheeting die. The die used (Fig. 21.11) is called a flat, slotted, or manifold type of die. The die has a steel body through which a $1\frac{1}{2}$ in. diameter hole has been bored, thus forming a manifold. The lower faces are machined at 90° to one another. These faces meet at a $\frac{1}{8}$ in. slot cut along the entire length of the die. The die lips are bolted to the die and can be adjusted by push-pull screws. All internal surfaces are smooth and highly polished. The electric die heaters can be of various types, but that in which a tubular heater is cast in aluminium alloy is

preferred. The heaters are located to form zones along the parallel (e.g. a die 90 in. long can have five zones). Approximately 200–225 w per linear inch of die are required to maintain the desired temperature.

It is preferable to have separate heaters on each side of the die rather than having semi-circular shaped bands designed to heat both sides from the one heater. With the latter considerable distortion takes place.

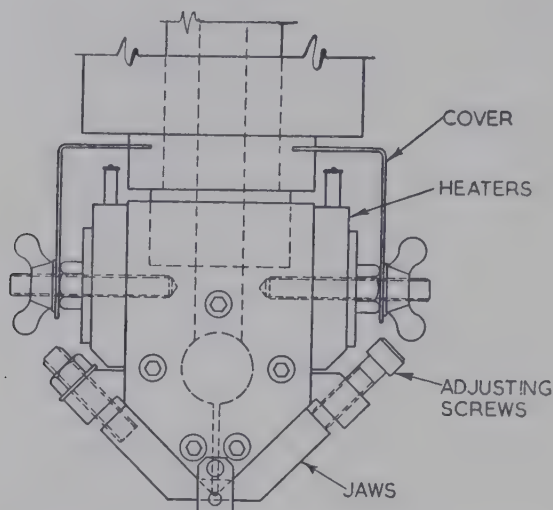


Fig. 21.11. Sheetting die for extrusion coating

making it difficult to obtain a uniform temperature gradient and therefore uniform extrusion along the length of the die.

Deckles consisting of slide wires are inserted in each end of the die to control the coating width. They are held in place by a small holder at the end of the die.

Laminating section. The essential parts of the laminating section are the neoprene roller and the cooling drum. The former has a hardness of 60–95 (Shore scale A), depending on the web being used, and is mounted in pivot arms connected to air cylinders. The cooling drum consists of a double shell roller through which cold water is circulated, and designed so as to provide good heat transfer from the outer surface. The temperature of the polythene coating is reduced approximately 250°C in its 270° angle of contact. The diameter of the roll depends on the rate of extrusion; an 18 in. diameter coating roll is required for rates up to 350 ft/min. and a 1 ml coating. Generally two gallons per minute, of water, are circulated for every kW of heat applied to the extruder barrel.

The finish of the cooling roll determines the type of surface on the product. Normally the surface is a highly polished, chromium plated one, although in some cases where a matt finish is desired this is obtained by sand-blasting or etching.

Adjustments are provided so that the cooling drum can be moved horizontally and the rubber roll vertically. By manipulating these two

adjustments the position of the die in relationship to the nip can be changed. On some occasions where it is necessary to cool the rubber this is done by running a water cooled steel idler roll against it or applying water to its outer surface. (Fig. 21.12.)

Various idler rolls are placed to lead the web through the machine. The diameter of these idlers varies and is determined by the flexibility of the type of web being processed.

Web handling equipment. Because of the different materials to which polythene is laminated it is necessary to supply types of web handling equipment which are suitable for the specific materials. The essential parts of the web handling equipment are the unwinder and rewinder.

A simple form of unroll stand (Fig. 21.6) consists of a shaft with cones, to hold the supply roll, riding in bearings and having at one end a friction type brake to control the web tension. Even with a twin unit of the simple type it is difficult to splice a fresh roll on to the end of the running roll

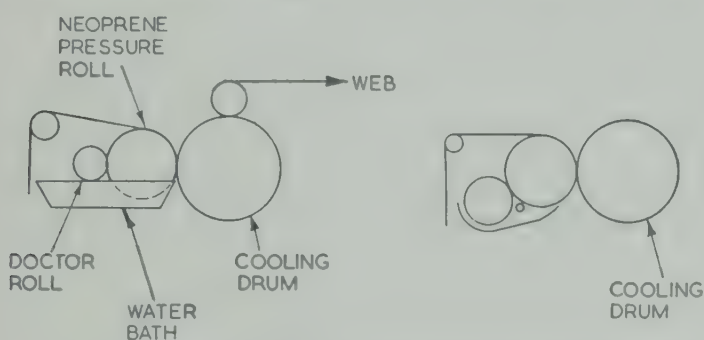


Fig. 21.12. Neoprene pressure roll, cooling and wetting methods

at the high speeds of production. For this reason the flying splice unroll stand is often used (Fig. 21.13). Another type of unroll stand containing a splicing mechanism is the turret type. This is only used in special circumstances, especially those where uniform tension control is important.

The winder is the equipment used to rewind the web on a core after the polythene has been laminated to its surface. There are two main types, the centre type winder (Fig. 21.6) and the surface type unit (Fig. 21.13). The type chosen depends on the web and whether the polythene is to be on the inside or the outside of the web as it is wound on the roll. For materials like polythene, glassine, Cellophane, and metal foils, centre shaft winders are usually used; for paper products surface winders are preferred. The centre drive type depends for its efficiency on the winding tension control. This will vary from friction clutches to hydraulic clutches and more complicated electric drives with electronic controls. Generally the centre winders are avoided where possible, especially for paper combinations.

Surface winders are of the double drum or single drum type, the latter being preferred because they are capable of continuous operation. Surface type winders have the advantage that the drums always run at

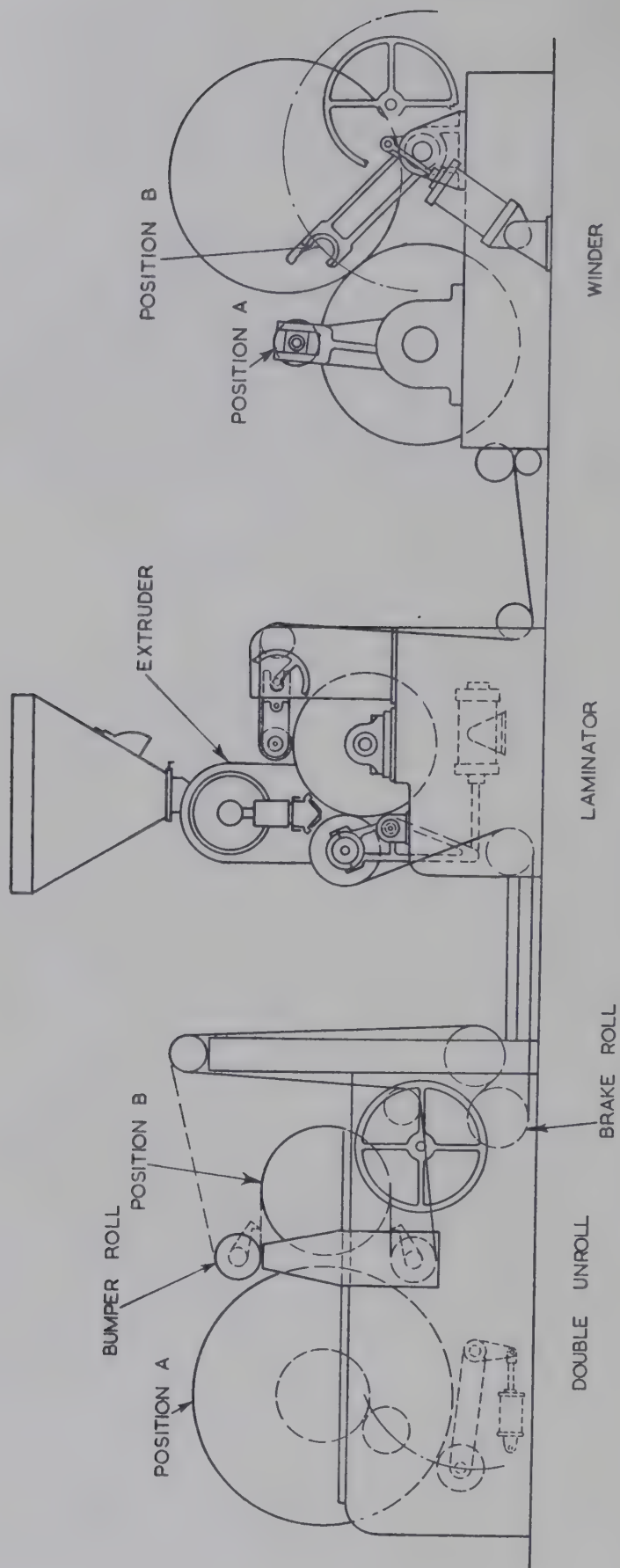


Fig. 21.13. Lay out of extruder, rolls and winder for extrusion coating

line speed and the weight of the roll and diameter build-up have only a slight effect on the drive characteristics. Winding speeds of 1000 ft/min are possible on a single drum winder.

Drives. Variable speed drives are required for both the extruder and the web handling equipment in order to regulate the coating thickness. The type of drive used will depend on the size of the unit and will vary from mechanical speed changers to an expensive installation controlling the speed of several DC drive motors.

Instrumentation. Instrumentation for temperature control is a very important part of the equipment. It is vital that the melt temperature of the polythene, and hence its viscosity, be accurately regulated as this effects the type of finish obtained and the gauge of coating extruded.

The simple type of on-off instrument is not satisfactory as the temperature fluctuation between the limits of its control is too great. A better quality instrument of the proportioning controlling type is necessary, preferably of the type in which the proportioning band is adjustable. The instruments for controlling the die temperature should be of the stepless type which produce even better regulation.

Since the adhesion in operating conditions depends upon maintaining a constant polythene temperature as it leaves the extruder and enters the die the use of a thermocouple located in the adaptor to measure the melt temperature is very important. Tachometers are available to indicate the screw and web speed; these are needed to determine approximate coating weights. Another useful instrument is the web break detector consisting of a light source and photo-electric cell between which passes the opaque web. When a break occurs in the web this causes the control circuit to open the nip by moving the rubber roll and also can be connected electrically to stop the laminator line as well as the extruder. This prevents molten polythene from being extruded on to the rubber roll should a break occur in the web.

Accessories

The following additional items, though not essential, are worthwhile incorporating in the unit:

A control panel in which all the control gear and instrumentation is grouped together assists the operator.

A method of moving the extruder and die in and out of the coating position is helpful, particularly for changing the setting of the die lips and carrying out other maintenance, especially on wide dies.

On large extruders operating at high outputs an automatic hopper can obviate a considerable amount of labour in feeding the extruder with raw material.

Expanders and edge guides are often used to eliminate wrinkles and position the web with respect to the laminator and the winder.

Because there is always a build-up of polythene at the edge of the web, edge trimmers or slitters are required. These are of two types, in which

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a sharp rotary knife runs against either the side of a wheel or in a groove against a driven hardened backing roll. The slitter wheels are spring loaded and are retractable to facilitate threading.

The trimmed off material can be disposed of by deflecting into a container or collecting box. A better method is to suck the trim into a tube and convey it away pneumatically. This latter method can incorporate a device for shredding the trim into small pieces.

In some particular applications it is necessary to preheat the web in order to remove surface moisture or to increase the temperature of the base stock in order to obtain better adhesion. This can be accomplished with banks of infra-red light, radiant heaters, or steam heated rolls. Care has to be taken not to overheat the web and remove too much moisture so as to weaken it or to scorch its surface.

OTHER TYPES OF LAMINATING

The process so far described covers the majority of installations where polythene is applied to one side only of the web. The next largest product made by this method is of a "sandwich" construction where polythene is put between two types of material and acts as the adhesive. For this there are two unwind stands, one located above and one to the side of the cooling drum. By bringing one web over the rubber roll and the other over the cooling drum the polythene can be applied between the two and laminate them together. The polythene produces a moisture-proof barrier; often two different types of material are used, such as paper and aluminium foil. In other cases, cloth, fibre glass, and jute are used to increase the strength of the product.

Occasionally there are demands for polythene laminated to both sides of the web. This can be done by running the web through the machine twice or by using two extruders and laminators in succession. Another process involves covering of an open web, such as cloth netting. Whether polythene is applied to open surfaces or laminated to both sides, care must be taken to ensure that the coated side does not mark or stick to the rubber roll. It is necessary then to cool the rubber roll externally as previously described.

USES OF POLYTHENE COVERED PRODUCTS

As previously mentioned, the main purpose of covering paper with polythene is to produce a moisture-proof barrier. This can work two ways, to keep moisture either in or out of the product which is being packaged.

The largest portion of polythene coated paper goes into the production of multi-wall bags. These are constructed with one wall or layer being of the coated product, the thickness of the coating depending upon the end use. Examples of products which are packed to keep them dry are cement, chemicals, dried milk, sugar and plastics. Examples where the packaging is used to keep the moisture in are pre-peeled potatoes, fresh

vegetables, meat and fish. Other uses of polythene coated paper are in building construction, covering concrete foundations, and the packaging of tobacco, machine parts, seeds and many other such products. It is often possible to use the coated paper for decorative purposes as the outside wrapping of cartons and boxes.

The combination of polythene with Cellophane, metal foil and glassine produces a unique material. The polythene adds moisture resistance while the base materials provide dimensional stability. In the case of Cellophane and polythene, the transparent product produced has many advantages. The polythene produces a heat sealing device from which pouches can be produced and sealed with heat at high production speeds. This application is useful for separating doses of pharmaceutical products, and individual servings of foodstuffs.

Hessians, cloth and meshes are laminated to polythene to produce moisture-proof bags, rainwear and coverings, used to make containers for motors, machine parts, and large items, many with military uses. In "sandwich" constructions the webs do not separate when they come in contact with water and are thus useful for panels and gaskets.

A number of special processes use polythene formulations incorporating various colouring materials, modifying agents such as wax, synthetic rubbers, and various molecular weight polymers. Some have better greaseproof resistance, while the wax blends have lower material cost and are used to compete with full wax coatings.

THE FUTURE OF PAPER COATED PRODUCTS

At present (1956) there are in the world approximately fifty production units with extruders of the $4\frac{1}{2}$ in. size and larger; in addition there are about another twenty-five smaller units. Their entire production capacities, if operated on a twenty-four hour basis, would probably consume most of the polythene produced at this time. With greater production capacity and a lower cost of polymer new markets are continually being developed. One of the most promising is the replacement of asphalt coated products by polythene. The adoption of polythene coated paper in place of asphalt coated products for building construction alone would increase the market by more than 50%.

At the moment the portion of coated material which is trimmed from the edge of the sheets is a complete loss, since the two cannot be economically separated and used again. In the newly developed techniques of extruding the polythene wider than the web and trimming only the polythene the waste can be eliminated, thus resulting in an appreciable saving which lowers the cost of the coated product.

There is also the possibility of using high density polythene to increase the grease resistance of a coated paper. The relatively poor grease resistance of low density polythene in comparison with some of the other materials has prevented its use with cosmetics and petroleum products. However, although not fully developed commercially, high density polythene of melt flow index 0.7 with coating characteristics similar to

low density polythene of melt flow index 7 has been applied to paper. The resulting material appeared to be tougher, have better grease resistance and a lower permeability to gases and vapours; also adhesion was very good down to polythene thicknesses of 0.001 inch. Although the tear strength of the new polythene is not quite as good as the standard material this is a less important factor compared with the apparent improvement in resistance to oils and fats and the better properties at higher temperatures. Another development which is relevant is the use of copolymers which can be printed, thus increasing the use of the product where applied to the outside of the package.

Taking all things into consideration it appears that the field of polythene coated products will continue to expand for some considerable time in the future.

ACKNOWLEDGEMENTS

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MANUFACTURING TECHNIQUES FOR BOTTLE PRODUCTION

M. FREUND

EVEN in the early days of the plastics industry various experiments were carried out to replace glass for bottle type containers. These designs—using two or more mouldings which were subsequently cemented or glued together—proved unsatisfactory and the production did not reach industrial significance. Thermosetting and thermoplastics materials were used, but all experiments remained in the development state until polythene became available. The introduction of this material enabled the industry to develop a new line of products. Due to the happy co-operation of engineers and technologists the production achieved a high technical standard and economy; the goods, produced by modern mass production methods, were economically priced and have found their way into our everyday life.

The development took place in recent years only, and Table 22.1 lists 20 patents referring to the subject, all issued in the U.K. during the period 1939–55. From the 20 patents issued 8 were originally applied in the U.S.A., 6 were originally applied in the U.K., and the rest in Italy, Germany, Rumania and Switzerland.

Four methods which are patented do not use any accepted commercial plastics machines for production—they refer to dipping or drawing and the parts produced thus are cemented or welded together. This production, as far as can be judged from the bottles available all over the world, did not reach commercial significance and the large majority of the bottles produced now are based on extruders and injection moulding machines.

In the following the main features of the principal bottle production methods from low density polythene are discussed:

(1) Injection moulding—

Closed preform and subsequent immediate blowing.

Injection moulded parts and subsequent heat sealing.

(2) Extrusion of tubular bodies with subsequent immediate blowing—

Extruder with one or more fixed nozzles.

Extruder with multiple nozzle and rotary feed.

Extruder with fixed single nozzle and rotary table with multiple moulds.

PRODUCTION ON INJECTION MOULDING MACHINES

There are two established methods of bottle production on injection moulding machines:

Injection moulding of preforms which, whilst hot, are immediately moved into the blowing cavity and blown to shape. The blowing cavity is either an integral part of the mould and the machine produces finished bottles, or blowing may take place outside the injection moulding machine. In this case the blowing cavity is located next to the machine and the preform moved by hand from the mould into the blowing cavity whilst the preform is still hot.

Parts of the bottle are injection moulded by conventional injection

Table 22.1. PATENTS REFERRING TO PLASTICS BOTTLES—
MACHINES AND METHODS

Date complete specification published	U.K. Patent No.	Firm or inventor	Type of machine	Date original application	Remarks
(1) 28.12.39	516262	Plax Corporation, U.S.A.	Extruder	21.7.38	Refers to cellulose acetate.
(2) 8.8.40	524534	C. Hubner	No machine	31.1.39	Cylindrical bodies produced by dipping or drawing are cemented and sealed onto suitable cover piece
(3) 8.5.41	536252	Monsanto Chem. Co., U.S.A.	Compression press	16.9.38	Cellulose acetate
(4) 25.9.44	564350	Plax Corporation, U.S.A.	Extruder rotary mould	9.6.42	Machine patented
(5) 19.7.50	640516	T. H. Craigie Blewis & Shaw (Plastics) Ltd., England	No machine	6.5.47	Welding or cementing parts to form a bottle.
(6) 27.2.52	667163	British Xylonite Co. Ltd., England	Extruder	9.5.41 U.S.A.	
(7) 24.12.52	684863	E. E. Mills, U.S.A.	Extruder	3.10.49 U.S.A.	Moulds on rotary table coaxial with extruder.
(8) 24.12.52	684611	T. H. P. (London) Ltd., England	Injection machine	28.11.50	Two or three stage process.

Table 22.1.—Continued.

Date complete specification published	U.K. Patent No.	Firm or inventor	Type of machine	Date original application	Remarks
(9) 21.1.53	686291	Novoplast G.M.B.H. Wallbach, Switzerland	Injection machine	15.4.50 Switzerland	Preform injection moulding subsequently blown into shape.
(10) 25.2.53	688021	Zareh Lorenian, Milan, Italy	Extruder or injection machine	14.8.46 Rumania	
(11) 18.3.53	688997	M. Biddulph Universal Metal Products Ltd., England	Extruder	22.12.50	Extrusion fed on air tube and trapped.
(12) 10.6.53	692590	Badische Anilin & Soda Fabrik Germany	Extruder or injection machine	7.12.49 Germany	Preform produced in first stage subsequently pushed into blowing mould.
(13) 12.8.53	695611	R. Colombo, Italy	Extruder	25.9.50	Rotating table.
(14) 23.9.53	697326	J. S. Walker, Fraser & Glass Ltd., England	Extruder	27.7.50	Nozzle opposite in line with extruded tube.
(15) 16.12.53	700984	E. Shipton & Co. Ltd., England	Extruder	11.9.50	Extruder with plurality of nozzles.
(16) 30.12.53	701638	Injection Moulding Co., U.S.A.	Method	17.11.50	Fusing the body portion with the bottom.
(17) 30.12.53	701639	Injection Moulding Co., U.S.A.	Sealing apparatus	17.11.50	Sealing method and apparatus.
(18) 10.2.54	703970	Friedrich Lorenz, Germany	Extruder	22.4.52	Nozzle formed by sleeve and plunger.
(19) 24.3.54	705971	C. V. Carlson, Cosom Ind., Inc., U.S.A.	No machine	12.12.51 U.S.A.	Heat fusing of moulded shells.
(20) 11.8.54	713419	Lacrinoid Products Ltd., England	Extruder	24.12.52	Blowing nozzle opposite extruded tube.

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Table 22.2. COMPARISON BETWEEN THE TWO-INJECTION MOULDING METHOD

Production factor	Preform with subsequent immediate blowing	Injection moulded parts with subsequent heat sealing
1. Accuracy of products	Tolerances peculiar to blowing process	More accurate products subject to injection moulding tolerances.
2. Tooling	More expensive due to blowing mechanism	As standard injection moulding.
3. Output of machine with respect to shot capacity	Up to maximum shot	Up to maximum shot.
4. Output of machine with respect to cycle time	Cycle time controlled by preform core temperature	Standard moulding practice
5. Finishing and assembly work	Minimum deflashing only, no testing required	Parts to be deflashed, heat sealed and 100% tested
6. Flexibility with respect to shape of bottle	Greatest variety of shape and design	Design restricted to injection moulding and heat sealing limitations.
7. Colour variations	One coloured, one piece products	Variations of colours of single parts.
2. Material used	Excess material used within economic limits	Excess material and scrap with standard moulding practice.

Table 22.3. DIMENSIONAL COMPARISON OF BOTTLES PRODUCED BY INJECTION MOULDING

Dimension	Preform with subsequent immediate blowing	Injection moulded parts with subsequent heat sealing
Volume of bottle cc	125	135
Weight of bottle gm	18	20
Weight per 100 cc gm	14.4	14.8
Wall thickness measurements on body—		
At top in.	0.044-0.057	0.045-0.055
At middle in.	0.044-0.061	0.042-0.051
At bottom in.	0.056-0.062	0.040-0.046
Base thickness in.	0.040-0.090	0.080

moulding technique and the parts are subsequently heat sealed and tested.

Table 22.2 shows a general comparison between the above two injection methods. Table 22.3 shows a dimensional comparison of specimens produced. These measurements—taken from average commercial products—show that the injection moulded and subsequently heat sealed bottles have more accurate dimensional consistency and less scatter at practically the same weight. The overall economy of the two production methods can be established only by close calculation of all factors involved.

Blow-moulding

It should be realized that the maximum single bottle size—in weight—is controlled by the shot capacity of the machine and with multiple cavity moulds the weight of the shot determines the number of bottles produced per cycle.

The mould, whilst basically following the ordinary injection mould design principles, primarily consists of three parts:

(i) Core and preform cavity for injection moulding. The core is bored for air supply with an air valve on the bottom end. The preform cavity is formed by two splits.

(ii) Blowing form, consisting of two splits which form the cavity or cavities, shaped according to the bottle required.

(iii) Mechanism or fixture—manually or mechanically operated to swing or move the preform (whilst sticking on the core) from the preform cavity into the blowing cavity. Usually the preforming and blowing cavities all mate in the same plane. The core swinging mechanism may be pivoted in the centre between the preform and blowing cavities; with such arrangements the moulding cycle is as follows:

Mould closing.

Injection of preform and pressure hold-on.

Mould opens and core swings from mould cavity into blowing cavity.

Mould closes with core in blowing cavity.

Blowing.

Mould opens. Core swings back into injection position (preform cavity) at half-way position, the moulding being blown-off from core.

The control of time, pressure and proper sequence of the single phases of the cycle remain within the scope of the engineering design. In all cases a degree of automation is being achieved, applying the usual electric time switches, combined with pneumatic or hydraulic pilot circuits. The reciprocating movements of the core—swinging from preform cavity into blowing cavity and back—are often actuated by mechanical means, controlled by the moving platen.

With the process as described above, the machine closes twice during each cycle—with other mould designs and controls injection and blowing take place simultaneously, i.e. the machine closes only once during each cycle. In the latter case the cycle time is controlled by the blowing time

(which includes cooling) and the overall time for the total cycle is reduced by approximately 20%.

More detailed information referring to the process is contained in literature¹ and Fig. 22.1 shows the characteristic features of the machine design, and refers to a method where blowing takes place outside the mould in an independent fixture.

A similar process, and also one without the core swinging attachment has also been described². The injection machine supplies a tubular blow the nozzle being adapted like a tube die as used on extruders. The split mould is directly closed on to the nozzle. The front end of

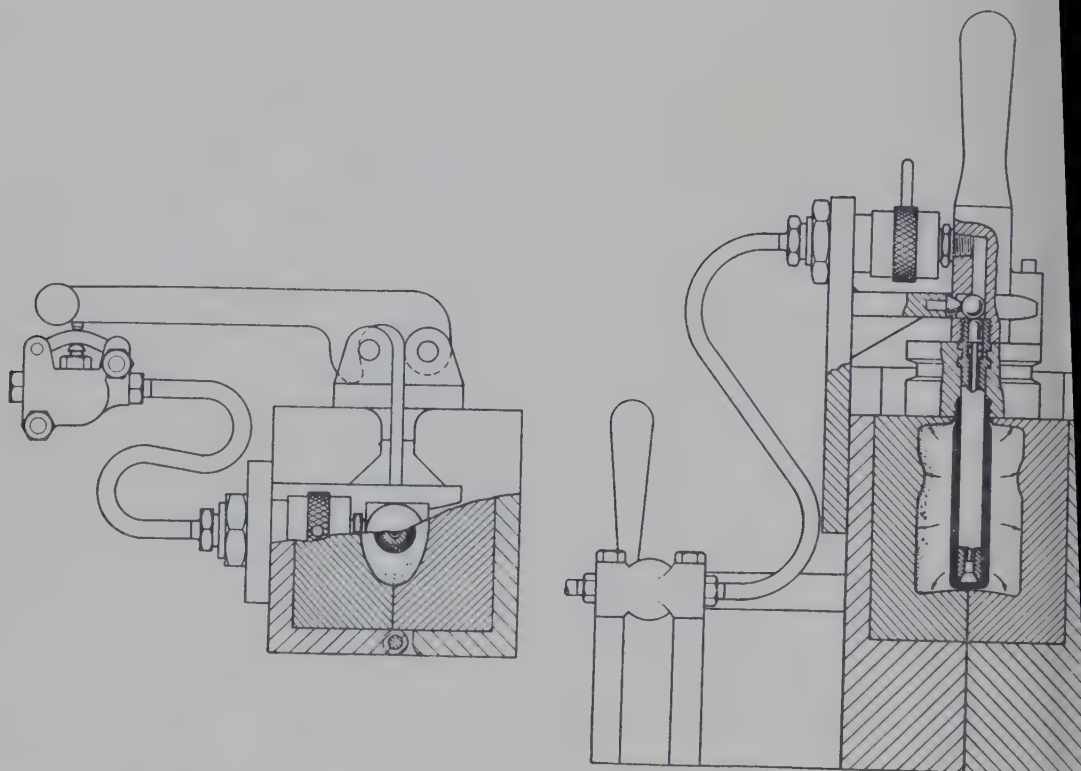


Fig. 22.1. Two views of the bottle blowing fixture to which the detachable blowing head assembly containing the hot injection moulded tube, is transferred from the injection machine

spreader or torpedo of the plasticising chamber is drilled for the compressed air supply required for blowing. Fundamentally this method works like an extruder—blowing die combination with single station, the speed of production being controlled by the cooling rate of the bottle die.

Injection moulding and subsequent heat sealing process

In this process the single parts forming the bottles, usually body and base, are produced by conventional methods. Plate 22.1 shows such a six-cavity body mould operated on an 8-oz standard machine.

The interesting operation is the welding of the base to the body. This operation is carried out on special heat sealing machines, sealing several

bottles simultaneously. The sealing die is electrically heated and pressed in the parts to be sealed; consequently the seal portions have to be shouldered.

After sealing, the bottles are subjected to air pressure. All these finishing fixtures are designed for mass production; a typical layout has been described.³

THE BLOWING PROCESS ON EXTRUSION MACHINES

All bottle making processes based on an extrusion machine work on the same basic principle. The extruder supplies a tubular body of the required section. A mould consisting of two splits is ready to receive a portion of the extruded tubular body. As this portion is trapped between the two mould splits, both ends of the tubular portion are closed and sealed. At this moment compressed air is being supplied through the neck portion and under this pressure the tubular closed body expands within the cavity.

By correct co-ordination of extrusion, mould closing time, temperature and air pressure supply, with subsequent cooling after blowing, a fairly consistent product is produced.

Based on this fundamental operation the machines and production methods show a great variety. The specimens produced are fairly consistent and the raw material used is rather less than with any other method. An average direct-extruded-blown bottle of 300 cc content and of diameter to length ratio 1:2 weighs 30 gm, i.e. 10 gm per 100 cc. The average wall thickness on the cylindrical body is 0.031–0.037 in.

The accepted production methods for bottle making—based on extrusion are:

(a) Extruder with one or more nozzles with controls for semi-automatic production, with stationary nozzle and portable moulds.

(b) As (a), but automatic.

(c) Extruder with stationary single nozzle feeding several moulds mounted on a rotary table.

(a) A typical machine is the semi-automatic Shipton model. Two nozzles—A and B—are attached to the extruder each feeding the corresponding moulds. A special control valve is fitted to the machine and the operation is as follows⁴:

Mould A is opened with the control valve left in the position which feeds material from the screw to the nozzle immediately above mould A. Sufficient length of material is then extruded and the control valve is operated so that the material from which the bottle has been formed is separated from the main mass of material by means of a cutting edge within the valve.

The valve is then in such a position that the flow is connected to nozzle B, through which the material will now be extruded.

Mould A is then closed and air applied through the core pin to extrude the material in conformity with the mould.

Then, when nozzle B has extruded a sufficient amount of material, mould B to be closed around it, air is applied through the centre of the core pin of mould B. The control valve is returned to the A position so that it is feeding nozzle A.

Mould A is now opened and the completed bottle is removed so that the cycle can re-commence.

With some combinations of bottles it is necessary to operate the changeover between cycles, so as to disconnect the supply of material to the valve.

With the above machine a vast variety of shapes and sizes can be produced in any capacity required up to 80 fluid ounces, which is equivalent to a 14-oz weight shot.

Wide- or narrow-necked bottles can be provided as desired, and both types can be produced at the same time.

As single- or multiple-impression moulds may be used, the tooling work required is the very minimum. In some cases it is possible to satisfy a customer's requirements with just one mould for his type of bottle, so that with the two-headed machine two customers can be supplied at the same time.

(b) This machine—a patented design, can accommodate up to 12 moulds at a time and thus manufacture 12 dissimilar bottles at rates up to 2,000/hour. The machine is still basically a two-station unit, but at each station six extrusion heads are provided.

A very novel feature of this machine is a fully automatic compensating device which allows for any variation in the viscosity of the material being fed through the nozzles, thus ensuring that each mould is supplied with the exact amount of material required.

Mould closing, blowing, opening and ejection are all completely automatic in operation and the machine has a plasticizing capacity of approximately 20 kg. per hour.

The machine (Plate 22.2) was built by E. Shipton & Co. Ltd., of Northwood, Middlesex, at whose works a battery of such machines is in operation.

(c) High production is achieved with machines based on an extruder—and several moulds—fitted on a rotary table. This extrusion blowing method⁵ which is a continuous process, has all the advantages of the glass blowing technique. One operator only, whose duty it is to keep the hopper full and occasionally adjust the size or rate of extrusion, is necessary.

The rate of production on a medium sized machine varies with the bulk of the object blown and has been over 20 per minute or 12,000 dozen per five-day week.

The machine described (Plax patent) is at the works of Cascelloid in Leicester. Plates 22.3 and 22.4 show the general arrangement. The

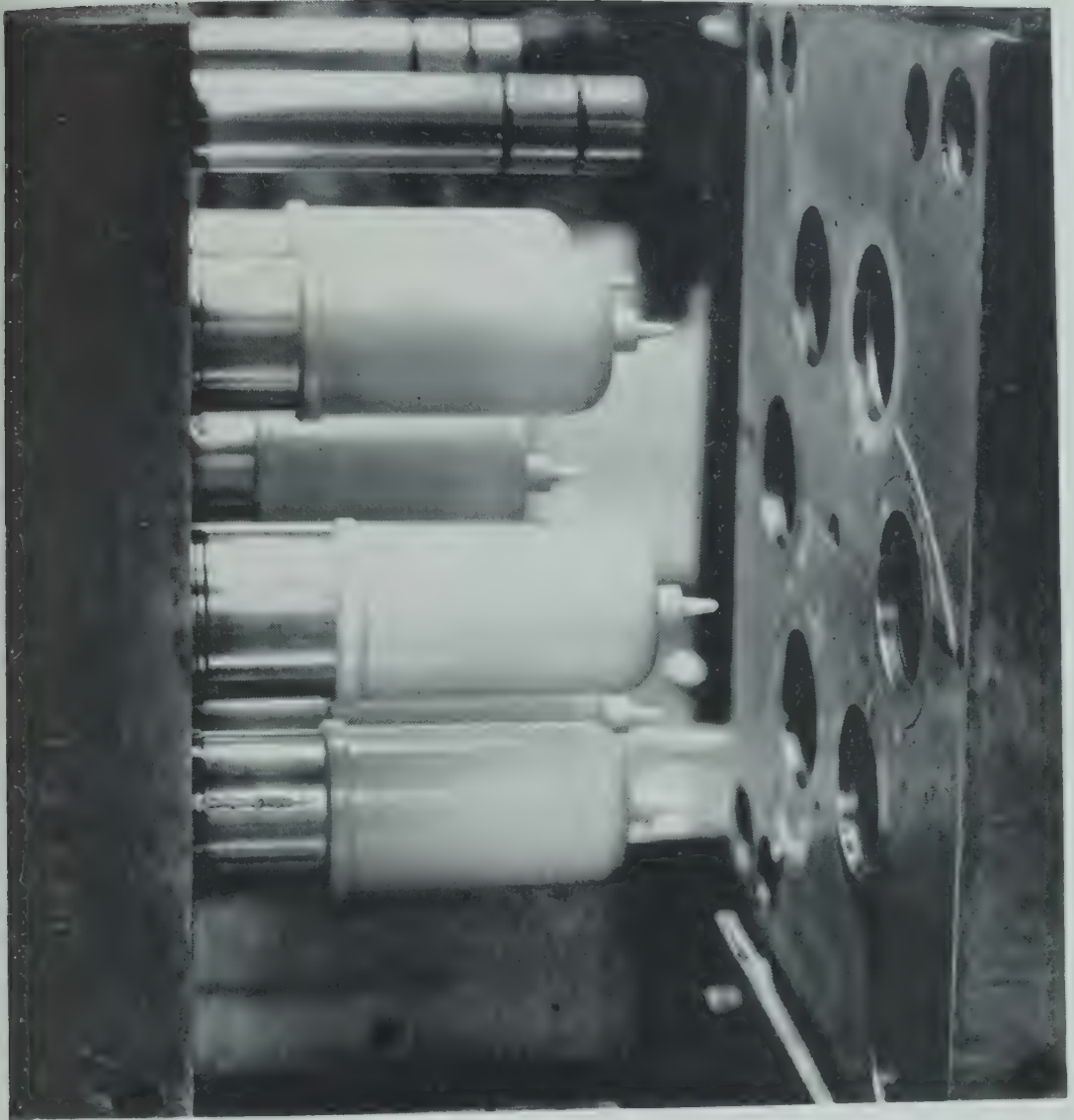


Plate 22.1. Injection moulding of bottles using six impression tool. Base portions are heat sealed in position in subsequent operation (Courtesy E. K. Cole Ltd.)



Plate 22.2. Sorting bottles from automatic extrusion-blowing machines (Courtesy E. Shipton & Co. Ltd.)

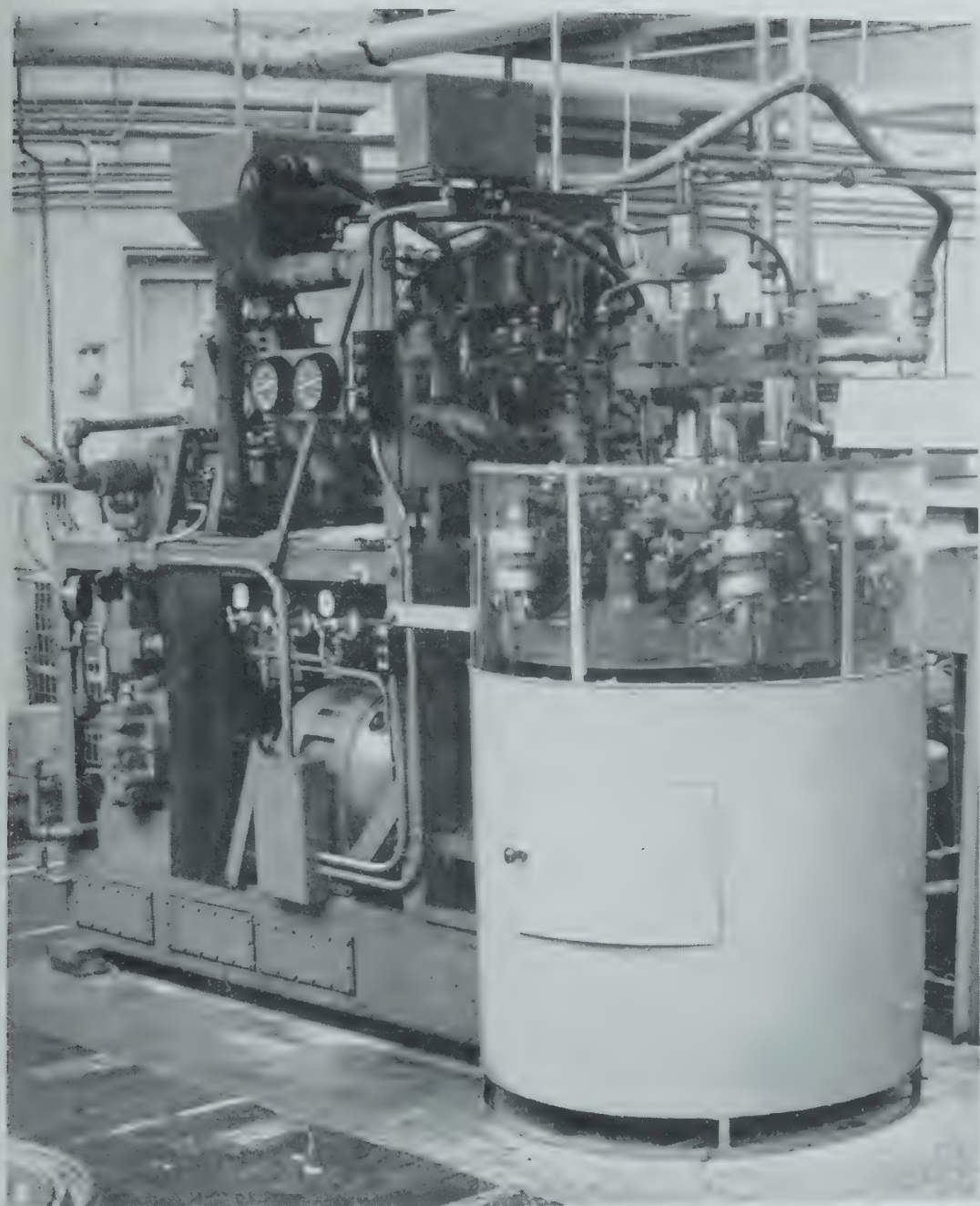


Plate 22.3. General view of extrusion-blowing machine with single nozzle feeding several moulds on rotary table (Courtesy Cascelloid Division of British Xylonite Co. Ltd.)

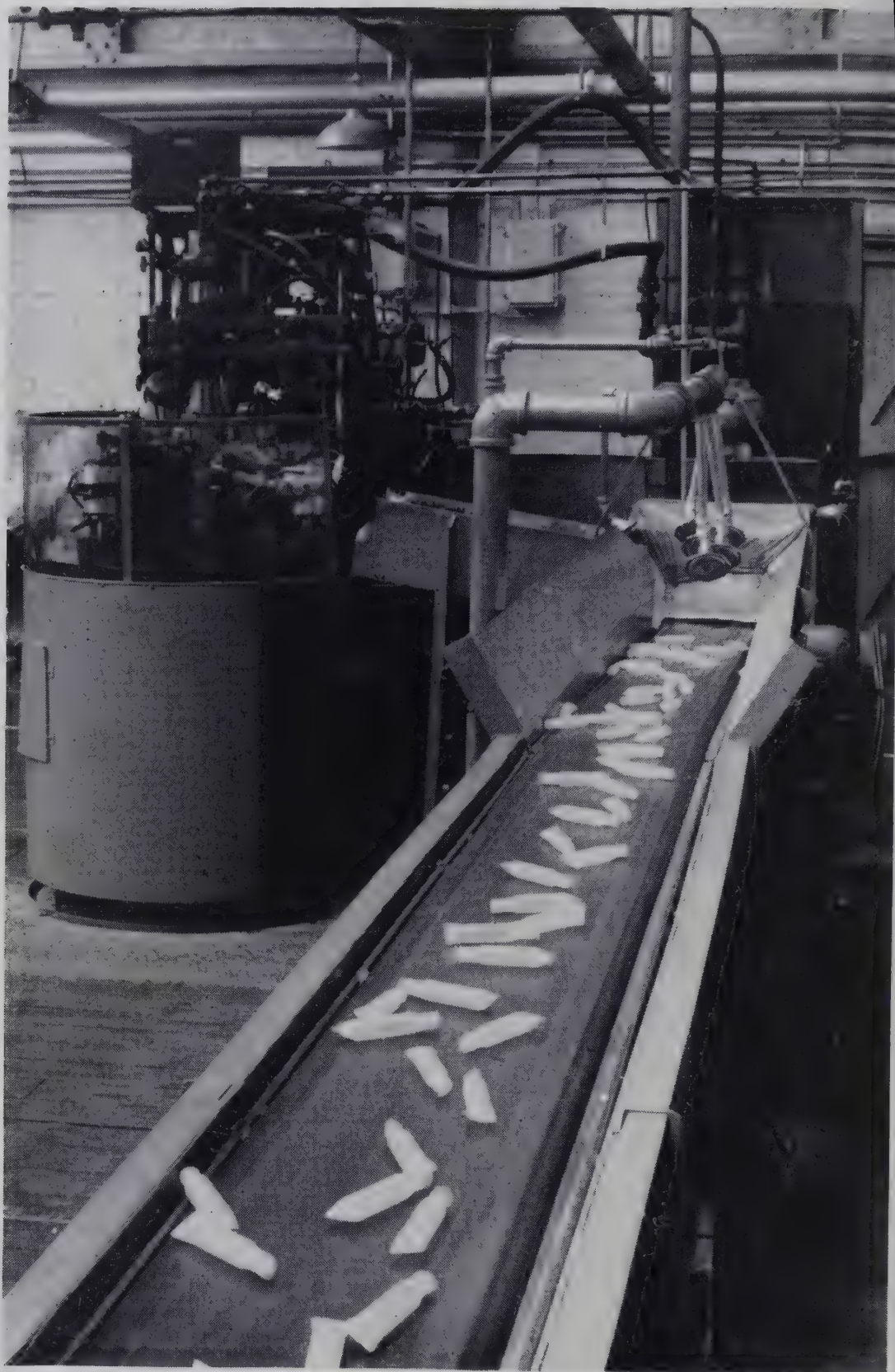


Plate 22.4. Bottles from machine shown in Plate 22.3 fall onto conveyor where they are cooled by water spray

hopper shown high up on the left-hand side in Plate 22.3 is filled with moulding powder which is fed at a predetermined rate to a horizontal cylinder. A piston compresses it, forcing it through the heating cylinder and finally extrudes it vertically downwards in the form of a tube through the nozzle attached to a vertical cross-head. Hot oil is circulated round the cylinder cross-head and die maintaining temperatures at the required level. The rate and size of the extrusion are so adjusted that, at the precise moment when it reaches its correct size an open mould, momentarily registered directly under the extrusion head, closes around the tube nipping the extreme end and thus sealing it and centralizing the hot plastics material.

At the same instant as the mould is closed, air is blown through the hollow extrusion, forcing it to assume the shape of the hollow mould. All these operations just described are carried out at the first station of the four station cycle which comprises the process. No sooner is this done than a knife severs the contents of the mould from the extruded tube. The mould when closed must be very close to the nozzle as otherwise the extrusion would tend to inflate and perhaps burst above the mould. To make room for the knife, therefore, the whole extrusion head and cylinder are hinged at the rear and are momentarily raised to allow the knife to operate. Due to the air pressure in the soft extrusion between the nozzle and the mould a small flange of the material is left on the top surface of the closed mould. This serves two useful purposes—it prevents the plastics in the mould from falling through the apertures in the mould and it provides means for applying more air pressure to the blown product while it is cooling.

As soon as the tube is severed, the mould passes to its second station while a new open mould takes up its position beneath the extrusion head. While travelling to the second position a pneumatic pressure cap drops on the mould applying air pressure and remains there while the mould travels through station 3 until it is opened at station 4. At station 3, the mould is still closed with air pressure maintained.

Throughout the whole cycle the moulds are cooled by circulating water through flexible pipes so that by the time the full mould reaches the fourth station, the moulding is rigid enough to be discharged by an air jet which operates as soon as the mould opens. There is still considerable heat in the moulding, especially if it is bulky, and the ejection of the blow is arranged on to a conveyor over which cooling water can be sprayed through roses.

The discharge side of the machine with the take-off conveyor is shown in Plate 22.3. One tube is shown about to be ejected down the chute to the conveyor.

No water is being sprayed because the objects, being small, require no further cooling. The vertical knock-out pin which breaks the bottle loose from the mould can be seen.

Most blown objects and all bottles require a finishing operation which comprises trepanning the neck and tearing off by hand the small amount

of flash at the base. This can be carried out on the discharge coil or away from the machine, as desired.

PRODUCTION OF LARGE BOTTLES

Bottles up to 2,500 cc are normally produced by the methods mentioned—the only precaution being that the extruder or injection machine capacity must be sufficient to extrude or inject the specimen and the heating capacity of the particular machine must ensure continuous supply of homogeneous material. In this respect the basic considerations are the same as with normal injection moulding or extrusion production problems.

Large bottles or containers over 2,500 cc are usually produced either by large extruders or injectors built for the specific purpose, or by welding and fabricating using conventional methods.

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2. *Plastics*, 20, 114 (1955).
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4. *Plastics*, 19, 250 (1954).
5. *British Plastics*, 23, 98 (1950).

CHAPTER 23

SPRAY COATING

G. H. JENNER

POLYTHENE sprayed coatings are finding an increasing use in industry. Tanks which hitherto had to be fabricated in expensive stainless steels or nickel alloys can now be made in mild steel and subsequently coated with polythene. Experience is showing that polythene coatings are superior to polythene liners where the polythene is only partially held to the surface of the metal. In practice polythene liners almost always fail due to the differential expansion of the tank and the polythene causing buckling and eventual rupture of the lining. Sprayed coatings do not suffer from this disadvantage. Furthermore, polythene may be sprayed on to a complicated surface where it would be very difficult if not impossible to fabricate a suitable liner.

A further aspect of the advantages of polythene coatings arises from the fact that one may take a standard item such as a tank, pump, fan, etc., made of mild steel which would perhaps be suitable for non-corrosive environments and by coating it, it can be transformed into an article which can be used in relatively heavy corrosive conditions, both acidic and alkaline. The alternative to this is to manufacture the article from some resistant metal, for example nickel or stainless steel. Both of these alternatives are very much more expensive than polythene coatings, quite apart from the fact that such fabrication would be a speciality and, therefore, subject to delays and difficulties in manufacture. There are even some instances where a tank has been coated with polythene although it is known that the polythene will be attacked by the liquid held in the tank to such an extent that the coating will fail and perforation eventually take place. Under the same conditions stainless steel tanks also fail and it is still cheaper to replace by a polythene coated mild steel tank rather than a tank fabricated from a stainless steel.

TYPE OF POWDER

Powdered polythene of melt flow index 20 is usually employed for spraying, and must conform to certain specifications. The specified range of particle size for flame spraying is shown in Table 23.1. Polythene powder is required within these limits in order that it may be made to flow through either a pressure fed system or a suction fed system.

Polythene of melt index 20 is chosen instead of a higher melt index because the lower viscosity of the molten product improves fusing after powder spraying, and it is much more difficult to obtain a smooth coating when the material is more viscous. Conversely, there are difficulties if

Table 23.1 POLYTHENE POWDER SPECIFICATION

Screen size *	Percentage of powder passing sieve
44	100.0
100	≤60.0

* British Standard 410, Test sieves.

the melt index becomes too low; e.g. when coating with nylon, the index of which is considerably lower than that of polythene, the difficulties associated with the running away of the molten nylon highlights.

Polythene of melt index 20 becomes brittle at -250°C but poly coatings have been successfully employed over a long period in refrigerators where possibly not more than -10°C is experienced. Poly coatings are not recommended for continuous service above 80°C although a number of examples have been recorded where a poly coating has behaved satisfactorily for short periods over 90°C .

SURFACE PREPARATION

Objects which are to be completely enveloped by a sprayed poly coating need the very minimum of surface pretreatment. In these cases such pretreatment is confined to degreasing the surface. With the exception of these completely enveloped objects, the most usual surface preparation is that of sand blasting or grit blasting. This is not only seen as a cleaning process but also produces a surface which gives a high adhesion of the polythene to the base metal. In part the adhesion of a sprayed polythene coating is dependent on the type of surface finish produced by shot-blasting. Experience has shown that steel grit of 40 (B.S. 410, Test sieves) gives very satisfactory results.

Depending on the size of objects being coated, blasting can either be carried out in a small hand cabinet or in a shotblast room. Shotblast machines are designed to extract the scale and dust produced in the blasting. The shot is automatically collected and returned until it loses its cutting power.

If the metal can be shotblasted, then it is suitable for polythene coating providing the melting point is not lower than that attained in the oven. The only time when this applies is with articles which have been soldered together with soft solder.

ADHESION OF COATINGS

The reason for the adhesion obtained with various metals is not thoroughly understood, but there seems to be some reason for saying that the very thin film of oxide which is formed on the base metal during the preheating treatment of the powder spraying process plays a considerable part in determining the adhesion of the polythene coating. Coatings applied to aluminium normally have a higher adhesion than coatings applied to mild steel. There is, therefore, some evidence that

reaction takes place between the polythene immediately in contact with the metal surface, either via the oxide or in some other way, and this reacted polythene gives rise to the high adhesion values.

B.P. 750,645 deals with small additions, i.e. 0.5% to 2% by weight of anatase titanium dioxide to polythene for increasing the adhesion of the polythene coating at temperatures below 218°C on the initial preheat temperature. It is claimed in this patent that when such additions of anatase titanium dioxide are made, highly adherent coatings are ensured when the metal surface is heated to between 150°C and 218°C, whereas without such additions temperatures of 218°C up to 275°C are necessary in order to achieve this.

A perfectly adherent coating of polythene is one in which the adhesiveness of the film of polythene at room temperature is substantially equal to its cohesiveness. In other words, any attempt to strip a polythene coating at room temperature results in tearing a portion of the layer rather than separating the layer from the base metal. The small additions of titanium dioxide, therefore, are said to fulfil the function of controlling the oxidation of the polythene at lower temperatures without encountering any corresponding degradation which may be obtained at higher temperatures.

Providing the properties of the polythene itself are not changed with time, the adhesion of the coating remains the same. It is only to be expected that where the physical properties of the polythene are affected by contact with certain media, the adhesion will be affected. In such circumstances, polythene would hardly, in any case, be considered as a suitable protective coating.

SPRAYING METHODS

There are at the present time three general methods of spraying polythene. These are (1) Powder spraying, (2) Flame spraying, (3) Dispersion spraying.

The most widely used method is that of powder spraying. Articles will normally be considered for powder spraying unless there are some special features about the article which prevent that method from being used. One determining factor when considering powder spraying is the size of the object. There are many small objects and open articles which are more suitably and more economically coated by dipping (see Chapter 24). Tanks and objects having a considerable surface area, but not too large for the oven, are normally coated by powder spraying. Flame spraying is normally only used when the article is too large or cannot be brought to the oven. Dispersion spraying is most suited to thin coatings on the insides of tubes. The basis on which one chooses one method in preference to another is that of experience considering the limitations of each individual method.

The deposition efficiency by flame coating is 75% and the deposition efficiency by the powder method is approximately 85%. In both cases the powder which does not adhere to the article is not burned up but

simply misses the target and if collected may be resprayed by the same method. In the case of flame spraying a very small amount is burnt but this is probably not more than a few percent and consists entirely of the ultra fine material in the powder. The polythene put on the work is not oxidized or degraded and retains the properties normally associated with polythene.

Powder spraying

This method is similar to dip coating and "fluffing" where the object is heated to a temperature slightly higher than the melting point of polythene and then the powdered polythene is sprinkled on to the object. The excess powder is blown off and then the object is reheated in an oven in order to fuse the polythene coating. In the case of heavy coatings on objects of varying metal thicknesses, it has been found that such methods of application are not sufficiently uniform to give satisfactory coatings. A powder spray gun which dispenses the polythene powder evenly over the whole surface, therefore, has obvious advantages. This method of coating is very widely used and several automatic plants are now being constructed for the mass production coating of insides of containers.

Flame spraying

The technique of metal spraying by a flame gun is well known. Polythene spraying by the powder gun represents an extension of this technique. Continual research into flame spraying polythene has brought about ease

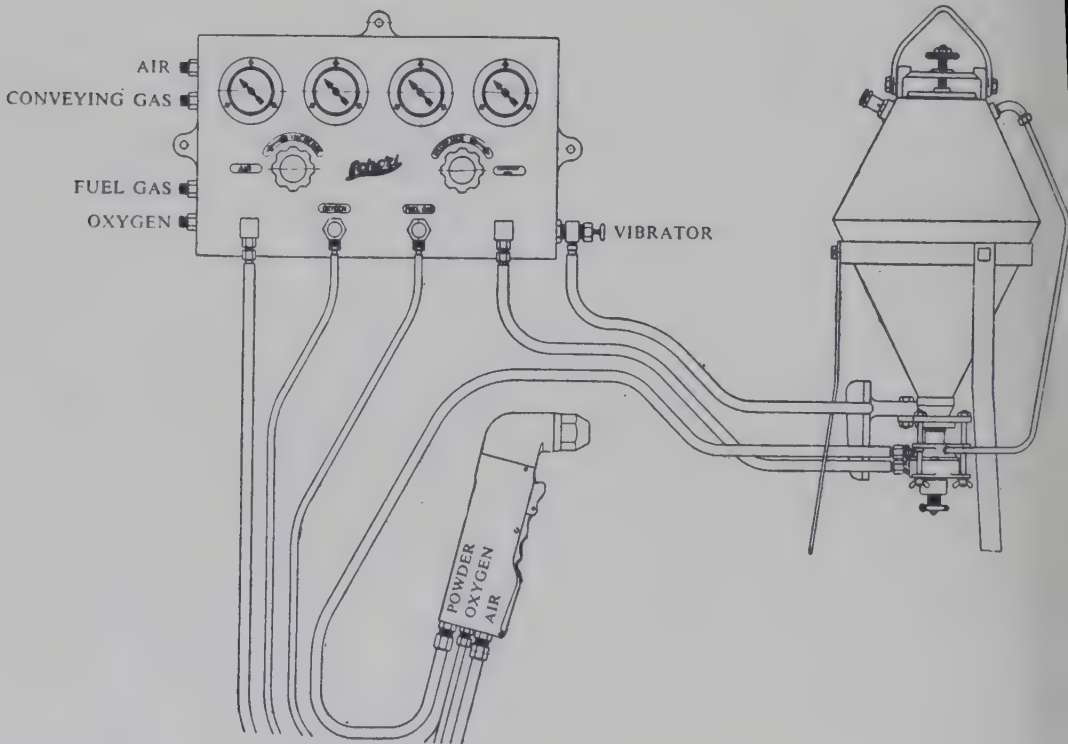


Fig. 23.1 Layout of typical equipment for flame spraying of polythene
(Courtesy Schori Division, F. W. Berk & Co. Ltd.)

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Table 23.2 OPTIMUM GAS PRESSURES FOR PRESSURE FED PISTOLS
(PRESSURES IN LB/SQ. IN.)

Type of fuel gas	Air	Oxygen	Fuel gas	Conveying air
Propane	15.0	25.0	2.5	10.0
Acetylene	10.0	15.0	4.0	10.0
Coal gas	20.0	10.0	3.5	10.0

and consistent polythene spraying and the ability to produce several different types of finish.

There are two basic types of pistol for flame spraying polythene, the induction fed and the pressure fed type. The pressure fed type is an improvement on the induction fed in that a more accurate control is possible especially if unskilled labour is employed. This type of pistol will be considered in detail. Fig. 23.1 shows a typical layout of equipment as used for flame spraying polythene. The equipment includes a control panel to which all gases are fed. The various pressures of gases required for correct operation of the pistol are set by means of regulators on the control panel. Powder is supplied to the gun from a separate unit which dispenses the powder in a compressed air stream. Typical fuel

Table 23.3 CONSUMPTION (CU. FT/HR.) OF GASES IN PISTOL

Air	.	.	270
Oxygen	.	.	77.5
Fuel gas	.	.	23.0
Conveying air	.	.	125

gases which may be used in this equipment include, propane, coal-gas and acetylene. A portable equipment is illustrated in Plate 23.1.

The supply of all gases to the gun may be varied by means of the control panel, and the quantity of powder supplied to the gun is determined by a regulating device on the bottom of the powder dispensing unit. It is, therefore, possible to control the nature of the flame, its velocity and that of the propelled powder thus giving optimum conditions for spraying. A salient feature of the pistol is that, having set the control panel and the dispensing unit to give the correct amount of gases and powder, depressing the hand grip gives the correct spraying conditions from a lit pistol. The pistol is so designed that, on releasing the hand grip, the powder supply is shut off and only a pilot flame remains. On depressing the hand grip again, full spraying conditions are established as previously.

Table 23.2 gives the optimum pressures for use in this type of equipment. Table 23.3 gives the consumption in cu. ft. per hour of the various

Table 23.4 SPRAYING PERFORMANCE OF PRESSURE FED PISTOL

Throughput	5.0 lb/hr
Spraying speed	80.0 sq. ft/hr.
Deposition efficiency	75.0%
Coating weight	0.076 oz/mil/s

gases supplied to the pistol. Table 23.4 gives the spraying performance with polythene.

In nearly all cases it is necessary to pre-heat the surface slightly to coat with the flame pistol to drive off all moisture. It has also been shown conclusively that coatings produced on a pre-heated surface have improved adhesion to the base. After this slight pre-heat, spraying is initiated by fully depressing the hand grip and working from one corner of the object to the other. A really large object may be sprayed by dividing the surface up into small areas and spraying the entire surface in a number of sections.

A typical tank coated by flame spraying is shown in Plate 23.2, and Plate 23.3 illustrates a polythene coated flame thrower with the crack finish. In the latter a small percentage of filler is added to give increased coating hardness and wear properties.

Dispersion spraying

Dispersions can be prepared by dissolving polythene in a suitable hot solvent (e.g. trichlorethylene) and adding a suitable alcohol (in which polythene is insoluble at room temperature). The polythene is precipitated in a finely divided form and remains in suspension; the dispersion is then used in this form. A type of polythene dispersion has been successfully developed suitable for producing thin and substantially pore free coatings of about 0.001 in. in thickness. Dispersion spraying of polythene is important because the thin coatings are produced at very low cost; it also lends itself to automation.

The polythene powder required for a dispersion is the finest obtainable, and in any case it must all pass through a 300 B.S. sieve. The proportions of solvent to alcohol in part determines the viscosity obtained and in general more dilute concentrations of dispersion give lower viscosities. An average concentration for spraying is approximately 25 to 30% polythene. The precise viscosity required for any particular operation will be determined by the spraying apparatus and also by the thickness of coating required on the individual job.

The dispersion can be varied in viscosity to meet individual applications for either dipping or spraying. In the case of spraying, conventional paint spraying equipment can be easily adapted. Immediately after the surface has been sprayed, the objects are placed in an oven and fused at a temperature of about 180°C. The fusing time depends on the size and nature of the objects being coated. Experience has shown that thin



Plate 23.1. Portable spraying unit (cf. Fig. 23.1)
(Courtesy Schori Division, F. W. Berk & Co. Ltd.)

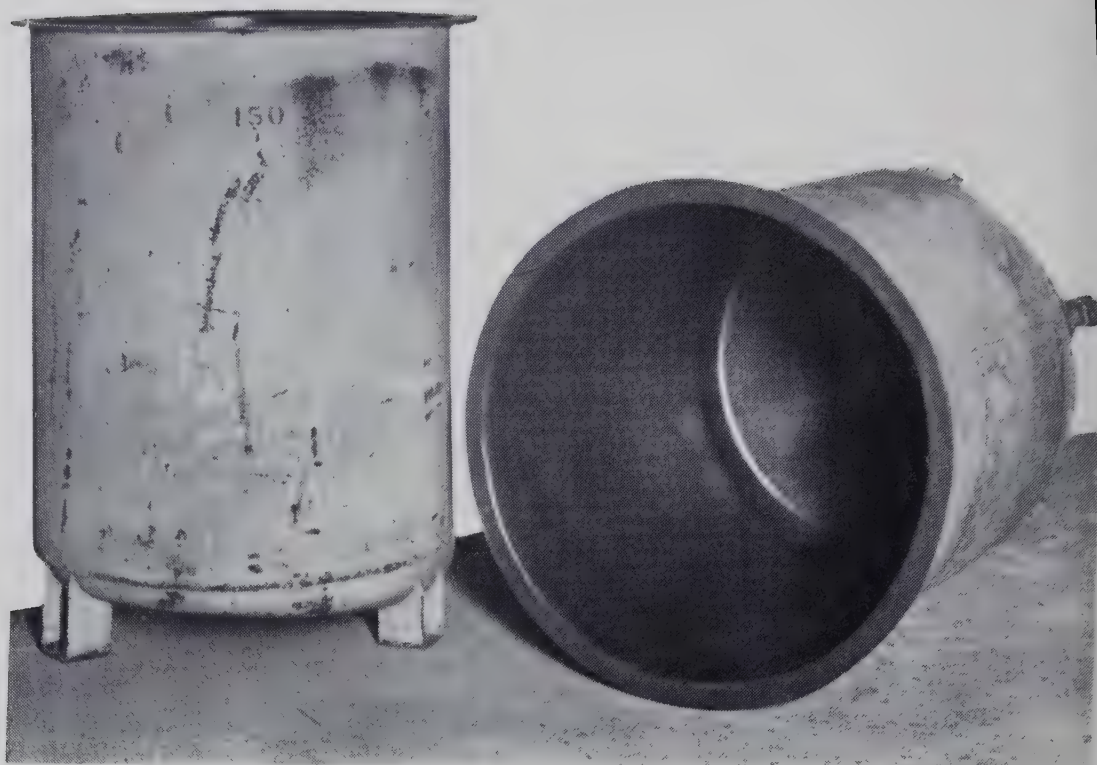


Plate 23.2. Tanks lined with polythene by flame spraying

Plate 23.3. Flame thrower container after polythene coating applied by flame spraying



copper foil can be sprayed and fused within 45 seconds. Other objects such as collapsible tubes can be treated within $1\frac{1}{2}$ minutes.

THICKNESS OF COATINGS

The standard thickness which is applied for all corrosive environments is approximately 0.020 in. Where pigmented polythene is applied for decorative purposes the coating may be substantially thinner than this, usually not more than 0.005 in., and in the case of coatings applied by the dispersion method thicknesses rarely exceed 0.002 in. and are usually approximately 0.001 in. One of the reasons for applying a coating of approximately 0.020 in. is that even if there is some absorption of the medium by the polythene to the extent that a certain amount of swelling or softening occurs, this will most probably be limited to a small fraction of the total thickness of the coating and, therefore, the great mass of the coating will not be affected. For example, a 10% softening of a film 0.005 in. thick may lead to its early rupture and failure, whereas with a coating 0.020 in. thick a 10% softening of the top 0.005 in. will have almost no effect. As a general rule for corrosive environment 0.020 in. is considered as the minimum satisfactory thickness and coatings considerably in excess of this thickness are sometimes applied. With decorative coatings the aim is, on the grounds of cost, to keep the coating as thin as possible consistent with it being perfectly pore free. Coatings applied to the insides of collapsible tubes must necessarily be fairly thin, otherwise the flexibility of the tube is affected, quite apart from the additional cost of the increase in weight of the polythene applied.

In each of the three methods described it is possible to continue treatments so that even thicker coatings are built up. In practice it has been found that under some conditions coatings much in excess of $\frac{1}{8}$ in. tend to be under stress and, therefore, are liable to crack. A fault to be avoided with all polythene coatings is to have areas of thin coatings adjacent to areas of thick coatings. Where extremes of thickness of coatings are adjacent, the thicker portion is stronger and either cracking occurs at the boundary between the thick and thin portions or the coating takes up a shape which has less surface area than the original. For example, on an angle it is possible for the polythene in the corner to contract away from the base metal.

The minimum coatings which can be applied are solely dependent on the amount of porosity that can be accepted in the finished job. In heavy corrosive environments a polythene coating must be completely pore-free. It is possible to do this by the powder spraying method with relatively thin coatings, but from a practical standpoint a coating thickness of 0.02 in. can be relied upon to give a pore-free coating. In the case of the very thin coatings applied to the inside of collapsible tubes, a certain amount of porosity may be tolerated depending on the commodity which is to be held in the tube. Flame sprayed coatings may also be pore-free at thicknesses less than 0.02 in., but because

of the general conditions outlined above a thickness of 0.02 in. is generally considered as the minimum.

TESTING SPRAYED COATINGS

It is obvious that since polythene coatings protect by sealing off the base metal from the corrosive environment even a minute pore can cause corrosion of the base metal and quickly spread below the coating leading to rapid failure and perforation. Early tests involved applying an H.T. supply to the insulation between the coating surface and the base metal. In one such test a p.d. of 240 volts was applied between the base metal and a damp brush. On passing the brush over the surface current flowed at any break-down, indicated by a deflection on the ammeter.

Closed vessels may be conveniently tested by filling with water and then conducting an insulation test on the vessel to ensure a perfect pore-free coating.

An alternative test for the coating is a high frequency spark tester which is similar to those used in the high vacuum industry. By suitable adjustment of the output voltage a spark appears on the end of the probe when a pin hole in the polythene coating is encountered. When using an instrument of this type the output voltage of the tester should be adjusted to suit the coating thickness, otherwise the voltage may be sufficient to break down the coating and ruin an otherwise perfectly pore-free coating.

A more recent development is the use of a high frequency tester, where a neon tube is built in the circuit to indicate current flow whenever a pin hole is located. Rod or spatula probes may be fitted to the tester and used in a normal manner.

Any pin holes discovered by this testing procedure may be repaired either by spreading dry powder on to the pin hole and fusing it in with an electric iron, or by flame spraying the area containing the pin hole with additional polythene.

FUTURE DEVELOPMENTS

Latest developments include equipment with higher throughput by which it is possible to spray large areas more easily. The day is not too far distant when a bridge will be coated in pigmented polythene. A new improved pistol known as the transposed air-gas pistol oxidizes less of the powder and gives more uniform coatings. Polythene dispersions have only just begun to be commercially available and it is probable that they will find a wide use in mass produced articles.

The importance of high density polythenes, with melting points considerably in excess of 100°C, is considerable, as there appears to be an extensive need for coatings with the chemical resistance of polythene which will stand temperatures just above the softening point of the present low density polythenes.

Another interesting new development is the irradiation of the normal polythene powder. Such irradiation treatment modifies the structure of

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the polythene and produces a material with a higher melting point which again is in excess of 100°C. Such irradiated polythene powder has been sprayed by both methods and satisfactory coatings have been obtained in each case. It, therefore, seems likely that, when these new materials are freely available, coatings of polythene may be recommended for temperatures higher than those which it is possible to recommend a polythene coating today.

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3. B.P. 643,539 and B.P. 643,691.

CHAPTER 24

DIP COATING

H. F. WILSON

BECAUSE of its chemical and physical properties polythene is ideal from many points of view as an insulation and anti-corrosive covering for both plain and intricately shaped metal articles. It is well known that the granules (the form in which polythene is supplied by its makers), being thermoplastic, can be fused together by the application of heat, and thus "cast" articles may be made merely by letting a mass of these granules flow together under the action of heat in a suitable mould. Another application of this principle is to take a metal article, heat it to about 180°C , and apply polythene granules to the exposed surfaces so that the polythene sticks to the hot metal wherever the granules touch it, and subsequently fuses into a homogeneous covering. In this way a skin of polythene encases the article.

Now the rheological properties of polythene are such that granules of conventional size, say $\frac{1}{8}$ in. cube, cannot be made to adhere to intricately shaped articles, or to flow into a thin skin. It has been found, however, that when polythene is finely divided i.e. reduced to a powder with particle sizes of less than 40 mesh, satisfactory coverings can be produced with thicknesses ranging from 7 mils to 40 mils or more according to the technique used for applying the powder.

It was as early as 1940 that a patent was filed (B.P. 571814) for converting polythene into fine powder form, but it was not until 1946 that the material was available commercially—at which time it was in demand for making decorative coloured finishes on aluminium suitcases.

However, it was not as a decorative finish, but as an anti-corrosive covering that polythene powder found its next application. The protection of electro-plating jigs had for long been a serious problem, but the fact that chemically inert polythene could be used to insulate and hermetically enclose an intricately shaped article made it very suitable for this purpose. Jigs which previously had to be removed from service after a comparatively short life were found to have their useful life increased many fold when they were given a 50–80 mils coating of polythene. In addition to these jigs, all manner of articles such as fan blades for operating in corrosive exhaust fumes, and exposed metal fittings in chemical works, were treated either by the spray gun or by hot dipping in order to give them a protective coat of inert polythene. The consumer goods field then began to use polythene powder as it became more widely known, and soon a large variety of articles, particularly wire-work such as plate racks, soap dishes, flower pot holders etc., were coated with polythene.

THE PRODUCTION OF POWDER

In order to produce the powder, use is made of the fact that polythene is insoluble in all cold organic solvents, whereas it is readily soluble in certain hot ones. When a hot solution of the polymer is cooled below approximately 60°C the polythene is precipitated as a fine powder which can be filtered off and dried. This is the substance of B.P. 571814, the production of fine powder by precipitation, and it is obvious that there can be wide differences in the concentrations of solutions used and the methods by which the solvent is removed from the wet powder. After precipitation and solvent removal the powder must be sifted in order to remove coarse material and adventitious impurities.

Other methods for powder production based on mechanical grinding at sub-zero temperatures have been patented, but in all these methods cognizance must be taken of the melt flow index of the polythene.

The powder can be coloured in either of two ways*—the method adopted depending upon dispersion of colour required and the end use to which the powder is being put. The colour, which usually takes the form of an inorganic pigment rather than a dye, can be added prior to or after the precipitation process, and if the latter method is employed it is obviously advantageous from the powder manufacturing point of view because the natural coloured powder can be produced in large quantities while the colouring matter is merely tumbled in as necessary. For perfect uniformity of dispersion, however, it is necessary to have the colour mixed with the polythene before precipitation (B.P. 617052).

THE DIP PROCESS

As mentioned earlier, polythene powder can be applied to metal surfaces by either spraying or dipping, but it is difficult to draw a definite line between the two techniques. By "dip" coatings we mean those which are produced by completely dusting a warm article with polythene powder and subsequently fusing the adherent powder by stoving at an elevated temperature (B.P. 643539 and B.P. 643691). It may be that the cold polythene powder is sprayed on to the hot article, a technique known as "fluffing"—the spray merely being a convenient method of dispersing the powder, but for the purpose of this chapter this is considered to be a spray coating, and is referred to in Chapter 23.

Metal pre-treatment

The adhesion of polythene applied by either the spray or dip techniques to copper, brass and lead is comparatively poor, and whenever these metals are to be coated it is desirable to cover the whole article so that the coating will contract on cooling and grip the metal tightly. Sand or shot-blasting the copper and brass improves the adhesion, and the surface should, of course, be free from grease and oil.

Aluminium, provided it is clean and free from oils and grease, gives remarkably good adhesion unless it has a very highly polished finish.

* See also Chapter 5.

The oxide film on aluminium appears to be an essential feature in the formation of good adhesive coatings.

The adhesion to steel is improved by sand or shot-blasting, or by an application of a phosphate film or by the combination of both. Where it is desired to apply a phosphate film to steel the surface should be free from oil, scale or dirt.

Pre-heating the article

The prepared metal object to be coated is either placed in an oven or on a pinpoint stand, or suspended by some convenient means—for instance by a wire attached by brazing. Soldering of the suspension wire is not effective as the temperature of the oven is sufficient to weaken a soft soldered joint. Where a thick coating of polythene is desired the temperature can be raised to 250°C, the thickness of coating depending on the temperature and the mass of the metal article.

Dipping

As soon as the required temperature has been reached the article is removed from the oven and immersed in sufficient quantity of polythene powder to ensure complete coverage of the portion to be coated. It is advisable to work the article through the powder with a rotating motion for a moment or two in order to allow all parts to come in contact with it and pick up a uniform coat. On removal, any excess powder is shaken off. The powder melts when it makes contact with the hot surface, but due to the low thermal conductivity of polythene an unfused layer of powder builds up over the whole article. The object will pick up only an amount of powder which can be coalesced by the available heat.

Now it is obvious that there can be several methods of applying cold polythene powder to a hot article in order to produce the initial adherent coating. Mere dipping in a volume of powder suffices for demonstration of the process, but is not an economic production method. Application by means of a cold powder spray or by passing the hot article through a dust cloud are other obvious means of achieving the desired end, and patents have been taken out to cover various techniques for applying the powder to the hot article. A recent development makes use of the cold technique as follows. The powder is kept in turbulent suspension in a tank by using an inert gas forced upwards through a porous bottom. A special apparatus on this principle has been patented in Germany (Pat. No. 933019). Another method of applying powder is disclosed in B.P. 746179 and uses the principle of electrostatic precipitation. This method is particularly suited for a continuous process, for example coating metal sheathed cables. When the article is dipped into the powder very little resistance is felt, the impression being one of dipping the article into a liquid, and every part of the article comes in contact with the powder.

Fusing

Transfer is now made to another oven at a temperature of 140–160°C until the powder fuses to a smooth coat. It is obvious that the stoving

temperature will vary in accordance with the melt flow index of polythene used for making the powder. Additional coats can be applied by repeating the process of dipping immediately the previous coat has coalesced.

HIGH DENSITY POLYTHENE

High density polythene made by a low pressure process appears in powder form as an intermediate product, and if granules are required the powder must first be plasticized and subsequently converted to the granular form. Polythene made by the high pressure process does not pass through this powder stage during its formation.

Up to the present time polythene powder from the low pressure process has given very poor results when used in Britain and sprayed or dipped coatings made from this material have shown a strong tendency to brittleness and cracking, and to deterioration by the action of certain liquids owing to environmental cracking.*

Another difficulty when using low pressure polythene powder for conventional dip or spray coats is the fact that coloured effects can be made only by rumbling in the colours or pigments, and it has been found from long experience that the mere addition of colours to powder in this way gives, in many cases, a by no means satisfactory dispersion.

It is possible that these and certain other technical difficulties in connection with the use of low pressure polythene powder will be overcome in due course, and that satisfactory coatings—both natural and coloured—will be achieved.

SOME UNUSUAL APPLICATIONS

There are many occasions when multi-colour moulding cannot be carried out conveniently, but where the use of polythene powder can achieve delightful decorative effects when used in conjunction with conventional moulds. It is possible, for instance, to apply powder to embossed or engraved surfaces so that one colour picks out the engraved markings while a complementary colour is used for the main body of the moulding. Some bi-colour lettered labels for permanent immersion in sea water have been made on this principle for a very important project, namely, the first Atlantic submarine telephone cable.

The fact that polythene can be pigmented to look like human skin has also resulted in a special grade of polythene being used for making dolls' faces with a very realistic appearance.

Yet another unusual application has been to utilize the wax-like lubricating properties of polythene for interleaving vehicle springs. The separate leaves of the springs have been entirely coated by the dip powder technique before assembly, thus producing a spring which is not only self-lubricating but completely incorrodible. It is probable that cost is the only reason which holds back the general use of polythene for this purpose.

*See Chapter 10.

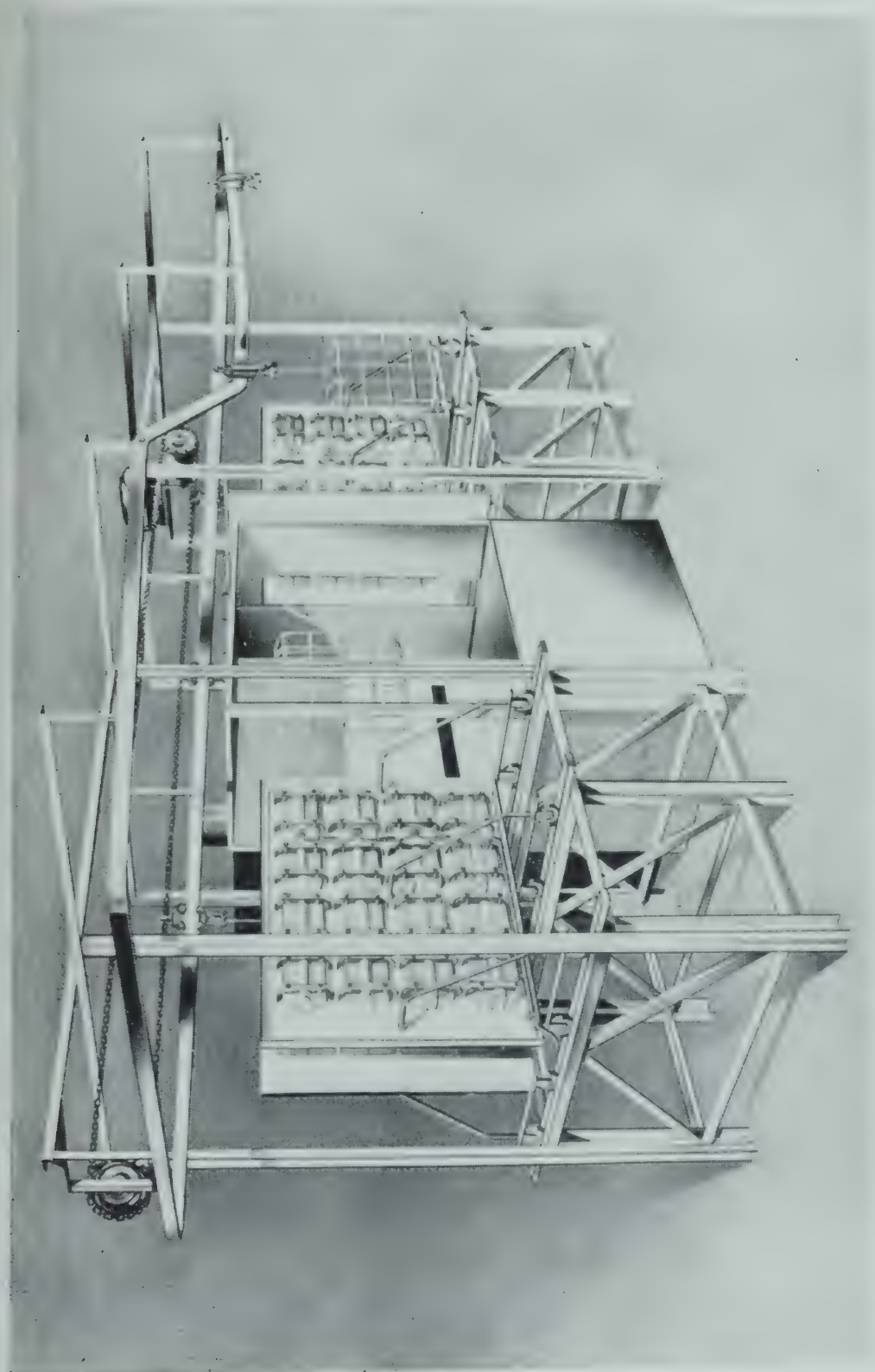


Plate 24.1. Continuous infra-red heating equipment Courtesy Schori Division of F. W. Berk & Co. Ltd.

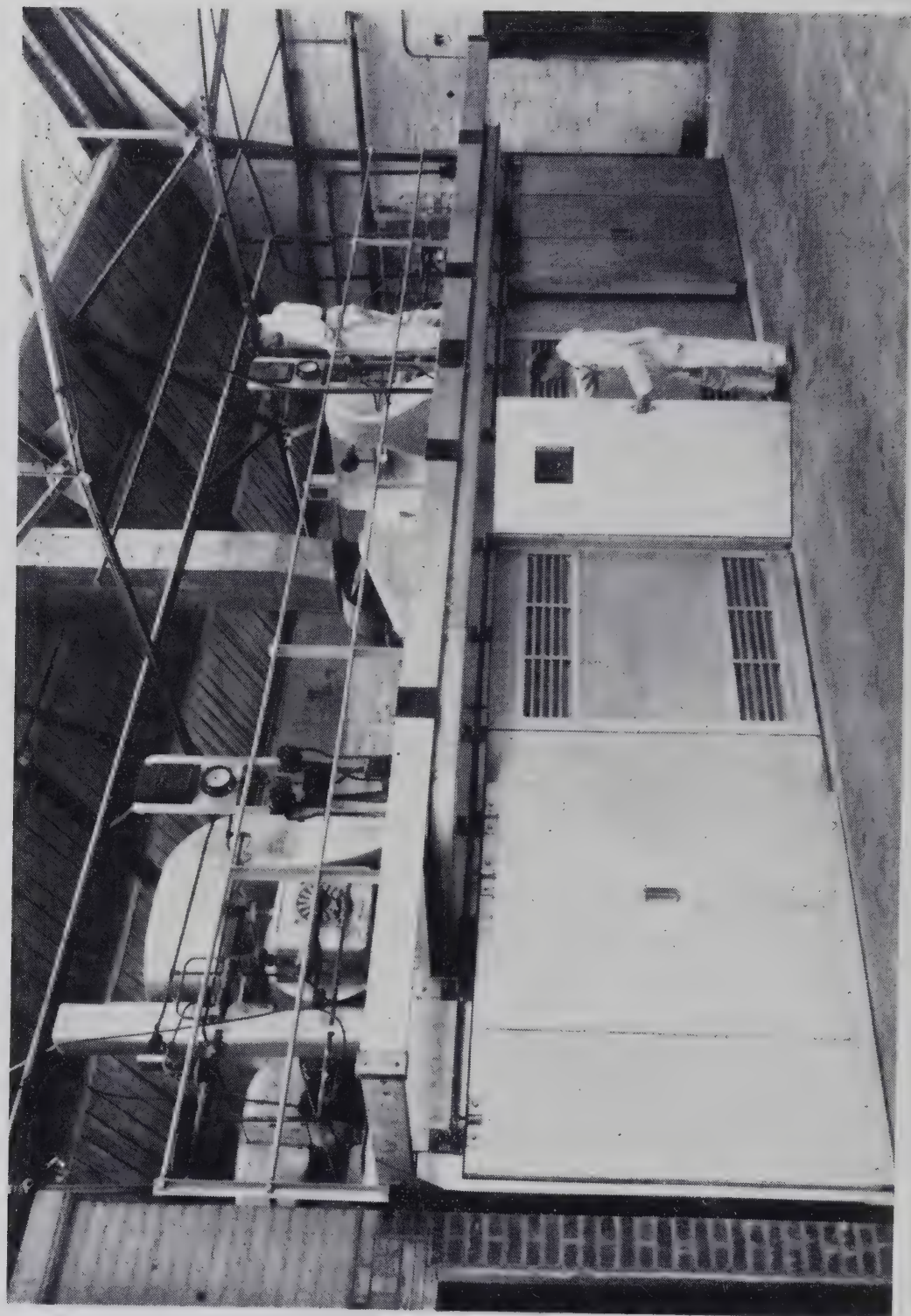


Plate 24.2. Oven installation for polythene heating (Courtesy Schori Division of F. W. Berk & Co. Ltd.)

PART III

APPLICATIONS AND PROSPECTS

CHAPTER 25

CABLES AND OTHER DIELECTRIC APPLICATIONS

R. C. MILDNER AND R. J. SLAUGHTER

THE range of cables in which polythene has so far found applications is very wide indeed. It covers the power cable field in which electrical energy is transmitted for domestic and industrial uses, for such purposes as lighting, heating, and motive power. It includes the field of communications; here the cable may be the sole transmission medium operating at audio or carrier frequencies, or it may be the link between radio equipment, receiving or transmitting, and the antenna. It extends to wiring and control cables in which powers are small, but requirements may be exacting. The voltages in these applications vary from a few millionths of a volt up to many thousands of volts and the current from a few microamps up to many hundreds of amps. Similarly the method of use of these cables can vary: in fixed installations the cable may be buried in the ground, pulled into conduit or cleated to a wall and not subsequently disturbed, whereas with mobile equipment the cables may be used as flexible leads and flexibility and lightness are primary considerations.

It is remarkable that the specific mechanical, electrical and chemical properties of polythene have all contributed to make it useful in some phase or other of almost every type of electrical cable. Cross-linking of polythene by some form of irradiation and the availability of high density polythene may well extend these uses in the future. Of course, the design of the cable may be influenced by the properties of the material available. Most applications for cable require a solid construction and for this purpose it is common to use the material in an extruded form. In certain cases, the polythene has been used in the form of mouldings or in the form of tape.

The various fields of application will now be reviewed to see the manner in which these specific properties of polythene have made its use attractive. They may be considered under the following headings: radio frequency cables; line communication cables; control cables and covered wires; power cables.

In addition to its use as a cable insulant the electrical and mechanical properties of polythene, as well as the ease with which it can be processed, make it an extremely useful material for other electrical applications. It will be convenient to discuss examples of these applications under the following headings: insulators for high voltages; low loss dielectric for

high frequency applications; low voltage applications where resistivity is important.

RADIO FREQUENCY CABLES

These cables may be either of coaxial form, in which the return conductor is disposed around the inner conductor, or of balanced type in which two conductors are placed symmetrically, with or without a surrounding earthed screen. The complete range of frequencies in which these cables are used extends from a few thousands of cycles per second up to about ten thousand million cycles per second. When used for receiving equipment the power to be handled is small but in other cases as for instance antenna leads for radar, radio-communication transmitters or broadcast stations or in such uses as radio-frequency industrial heating apparatus, the power may amount to many kilowatts. In radar equipment the energy is usually transmitted in short periodic pulses of power which may be of the order of megawatts.

The prime electrical characteristics which have dictated the use of polythene are its low permittivity and its low power factor. The low permittivity is useful because, for a cable of given characteristic impedance it permits the use of an inner conductor, large, relative to the overall diameter of the cable and thereby reduces the electrical loss due to the transmission of current through the conductors. The losses in the cable due to the electric field are proportional to the product of power factor, permittivity and frequency and therefore at high radio frequencies a low power factor is an important consideration. In those cases where high power has to be transmitted the high dielectric strength of polythene is a valuable characteristic. Similarly its resistance to deformation under mechanical load at high temperatures is important in the same context. In the maintenance of low power factor the chemical inertness of polythene is valuable by reducing the rate of oxidation during the processing operation. In terms of footage of cable the principal use of radio-frequency cables is as flexible leads between equipment or between the equipment and the aerial. For such flexible cables polythene has from the outset been used almost exclusively. For aircraft use few materials can match polythene in its ability to withstand flexing at temperatures lower than -60°C .

In common with other thermoplastics, polythene may be "expanded" by the addition of certain reagents which decompose to form gases at high temperatures. The resulting material has, of course, a permittivity lower than that of solid polythene, while it still retains a mechanical rigidity sufficient for all normal purposes. This makes it particularly attractive as a potential insulation for telecommunication cables.

Certain technical difficulties exist in the use of "cellular" polythene as the expanded material is called. Firstly the expanding agent must not leave any solid residues after decomposition as these would raise the power factor of the cellular material. Secondly the cell structure must be small and uniform and the cells must be non-interconnecting. The

latter requirements mean that extrusion conditions must be stringently controlled and the raw material must be a completely homogeneous mixture of the polythene and expanding agent. Cooling also presents a problem as if it is applied too suddenly the expanded insulation is likely to collapse.

Difficulties of manufacture have now, however, been largely overcome and cables insulated with cellular polythene can be produced with a permittivity of about 1.5. The power factor is still slightly higher than that obtained with solid polythene but there is every hope that it will be reduced in the near future.

Cellular polythene cables have found a ready use for domestic purposes as downleads for TV aerials especially on the new band 3 and they are beginning to supplant earlier methods of achieving the same technical result by means of a composite construction embodying substantial quantities of air. For instance, one early design of semi-airspaced cable, used for flexible leads has a thread of polythene wrapped around the conductor with an overall tube of polythene to provide a support for a return conductor. Alternatively a cartwheel construction of polythene was extruded in one or in two operations around the centre conductor. In cases where the return conductor is self-supporting the so-called air-spaced construction can be employed and a typical design of this type is the helical membrane cable. In other cases the insulating structure may be formed by discs or cylindrical thimbles of polythene.

LINE COMMUNICATION CABLES

Submarine cables

The use of submarine cables for the transmission of information in the form of telegraphy dates back more than one hundred years and until the introduction of polythene the insulant was a naturally occurring thermoplastic, gutta percha. Polythene has a certain similarity to gutta percha in respect of its rheological behaviour but in all the essential properties it is substantially better and therefore it has almost completely ousted gutta percha. Its permittivity and power factor are lower and its chemical inertness is of quite a different order. Furthermore the mechanical properties and in particular its resistance to deformation under mechanical load, even at room temperature, show a very big improvement over gutta percha. Robust and reliable joints are readily made in polythene core by injection moulding techniques.

In one respect only has the use of polythene shown a disadvantage over gutta percha and this is in relation to a phenomenon known as a knuckle fault. In laying or recovering submarine cable in deep seas the tensions on the cable are often very substantial and may in adverse circumstances exceed the elastic limit of the cable components. In such cases there is a permanent stretch of the cable and in particular of the copper conductor. When the tensile load comes off the cable the recovery of the armour may be greater than that of the copper conductor

with the result that the conductor tries to accommodate its length pushing its way between individual wires of the armour. When gutta percha was used as the insulant the gutta percha tended to accommodate itself to the copper conductor and remained as a water tight sheath around the conductor. This movement of the insulated conductor between the armour wires is known as a spew-fault. The elastic recovery forces are so great that, in the case of polythene, the conductor tends to pierce the polythene covering itself before issuing from the armour. This type of fault is known as a knuckle fault and is of course much more serious than a spew. Intensive work in recent years by submarine cable manufacturers has enabled them to design a cable which overcomes these difficulties.

The reliability of a submarine cable must be very high because the cost of repairing a fault is so great. For this reason the use of a synthetic material subject to strict control during manufacture has economic advantages over the use of a naturally-grown product which must be carefully refined, blended and tested to ensure products that will prove to be satisfactory.

In fact, the first full-scale factory trial of polythene in 1939 was in the insulation of one mile of coaxial submarine cable with the newly introduced material. Because the early polythene had very variable rheological properties a mixture of polythene and polyisobutylene in equal parts was used in the extrusion of this first length of submarine cable core. The preparation of such mixtures was described in British Patent 514687 dated Nov. 1939. Subsequent experience has shown that such a high percentage of polyisobutylene is undesirable and, when it is added to polythene today, amounts between 5% and 12½% are used. Certain advantages accrue from the use of such quantities, probably the two most important being the increased uniformity of extrusion resulting from the increased melting range of the mix and the improved resistance of the product to environmental or stress cracking.* A further advantage obtained from the use of polyisobutylene is that, owing to the possibility of extruding the mixed material at lower temperatures, less trouble is experienced with sheaths and "belts" sticking to underlying cores. With the softer grades of polythene the resistance to cold crack and shatter is considerably improved by the addition of polyisobutylene but with the hardest grades used today the position is reversed. One disadvantage of the use of polyisobutylene is the decreased resistance to deformation under load at elevated temperatures. For many applications this disadvantage is small and unimportant. In recent years polyisobutylene has in many cases been replaced by butyl rubber in polythene mixes.

The application of submarine cable has, with time been extended from telegraphy to telephony and there are already many links in various parts of the world in which multi-channel telephony is transmitted by means of carrier currents.

* See Chapters 9 and 10.

This development has enabled the first transatlantic 36-channel telephone cable to be laid. Although there are many details of considerable interest attaching to such a project, only those concerning the manufacture of the polythene core can be considered here. Prime requirements of cable for such a project are uniformity and stability of the electrical characteristics. The characteristics of the materials used in its construction have also to be accurately known for it is necessary to estimate the attenuation of the cable to very close limits. The low power factor of polythene facilitates this estimate, but the changes in its characteristics under varying conditions of pressure and temperature have to be obtained with considerable precision. The insulation of the cable is polythene of melt flow index 0.3 mixed with 5 % butyl rubber and a small quantity of antioxidant. This was extruded over an inner conductor consisting of a solid copper centre surrounded by three copper tapes. The extruder is of the modern cold feed type.

The diameter of the insulation is controlled during extrusion to very close tolerances by means of an electronic controller actuated by error signals from a diameter measuring device and a capacitance monitor. The gauge measuring the core diameter is placed near to the extruder and is arranged to correct rapid variations in diameter while the capacitance monitor is some distance away and corrects only long term variations, i.e. drift. It also provides a continuous printed record of the capacitance of the core during extrusion.

The preparation of the raw material for feeding to the extruder is of interest and is designed to ensure that any changes in the polythene supplied from the manufacturer should not result in a sudden change in the characteristics of the insulation of the cable. The polythene is mixed with the butyl rubber and antioxidant in a hot mixer from whence it is extruded in strip form. The strip is cut into cubes and in this form the material is pneumatically conveyed to five storage silos which have a capacity of 5 tons each. From the storage silos the material is fed to two mixing silos where it is thoroughly blended by passing pneumatically between the two. From there it is bled off in 1,000 lb. batches for passage to the extruders. During this process it is passed by conveyor belt through a metal detector. If any particles of metal are found a certain quantity of material is automatically rejected. By such methods a supply of pure, homogeneous, uniform material to the extruders is ensured.

In shallow-water applications for mining and other control cables, polythene is in many cases ousting rubber cables on account of its superior ageing properties.

Land cables

These may be of two types as in radio-frequency cable, namely coaxial and symmetrical cables. One point of difference in operation between line communication cable and radio-frequency cables lies in the fact that it is usual to provide in land cables a number of electrical

circuits, whereas with radio-frequency cable a single communication channel is usually all that is required.

In coaxial cable for line communications the emphasis on efficiency is such that so far only cables which are essentially air-spaced have come into general use. The internationally accepted design uses spacers and whereas originally these were made of ebonite, today they are almost invariably made from polythene although there are a few instances in which the spacers are made of polystyrene. The standard cable is $\frac{3}{8}$ in. diameter over the insulation. Where a larger diameter has been used the normal type of disc is not stable enough and in one notable case the insulation is built up from polythene mouldings in the form of semi-cylindrical shells incorporating a spacer to support the inner conductor.

The use of a solid dielectric insulation of polythene is very attractive in some cases, as for instance where the water level is very close to the surface of the soil or where additional robustness is required owing to the method of installation, as, for instance, with overhead lines, and it may be that in the future when the cost of repeaters is lower, their reliability higher and their maintenance lower than small cables of this type will come into use. One such cable was built and installed in Holland some years ago and has operated successfully as a television feeder. There are additionally certain other cases where solid polythene has been used on land as a continuation of a submarine cable system.

In the field of balanced cable, polythene-insulated multi-pair or quad cables polythene-sheathed have come into general use in this country as subscriber cable in which the radial thickness of insulation is of the order of 15 mils. It has been found that such constructions compete economically with the orthodox paper/lead cable in sizes up to about 25 pairs. Although certain advantages accrue from the use of a cable which will still operate even if the sheath is punctured the major consideration is one of economics. There are certain savings of course in installation in this case. For audio junction cable or for carrier-frequency cable where the electrical requirements are somewhat more severe and therefore require a somewhat larger wall thickness of insulation, it cannot be said that polythene has so far made very much progress as compared with the orthodox cables. However, a number of installations have been made in various parts of the world and their performance and economics are being studied with keen interest.

It seems likely that, with the advent of cellular polythene, the position will alter radically because with this material it is possible to equal or even surpass the electrical characteristics of paper cable of equivalent size and therefore the economical disability no longer holds. A number of developments are going on in this field.

Polythene sheaths have also been used with dry paper cores, either as reinforcement and corrosion protection to thin lead sheaths or in the so-called Stalpeth construction.

In this type of cable polythene is again used as the overall sheath but the construction of the metal screen is novel. The cable was designed

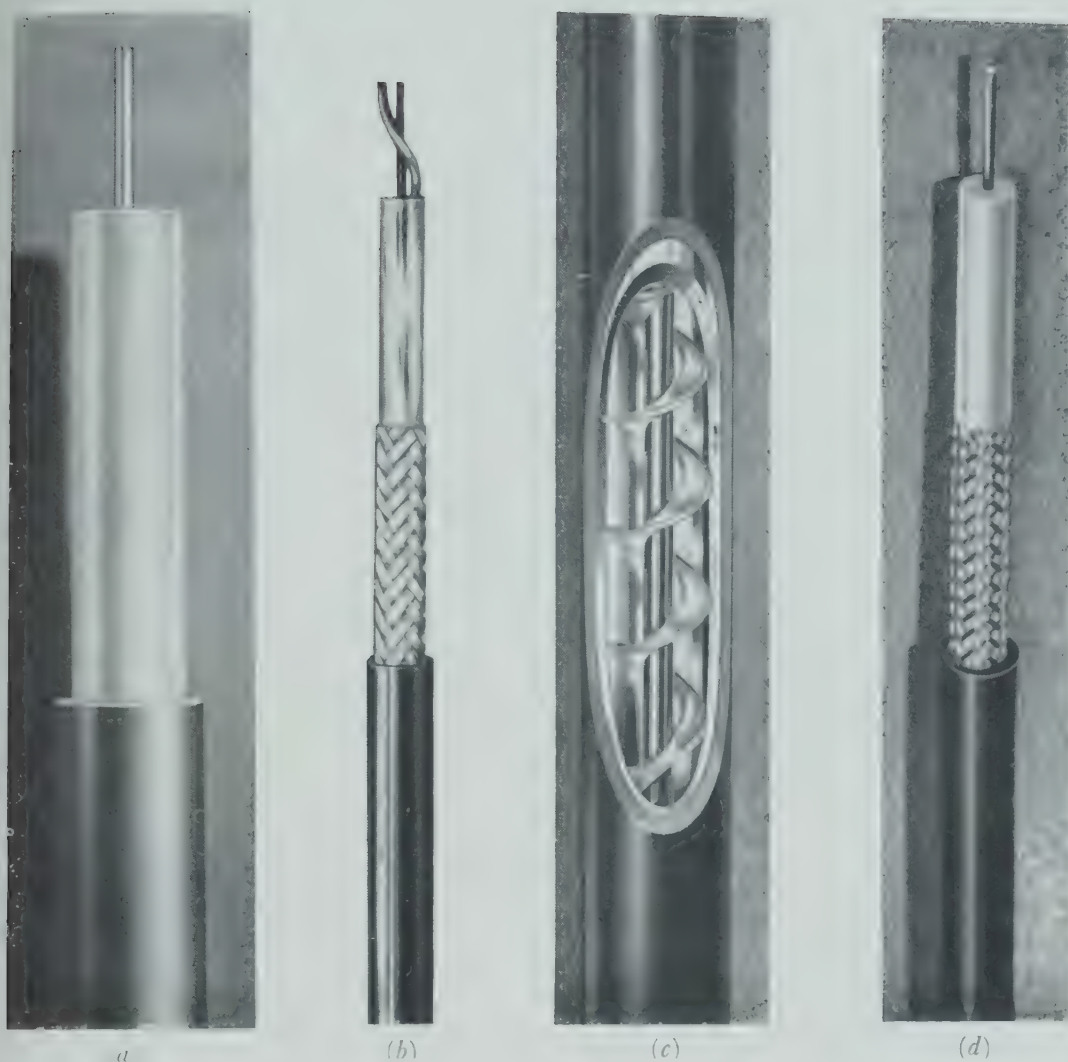
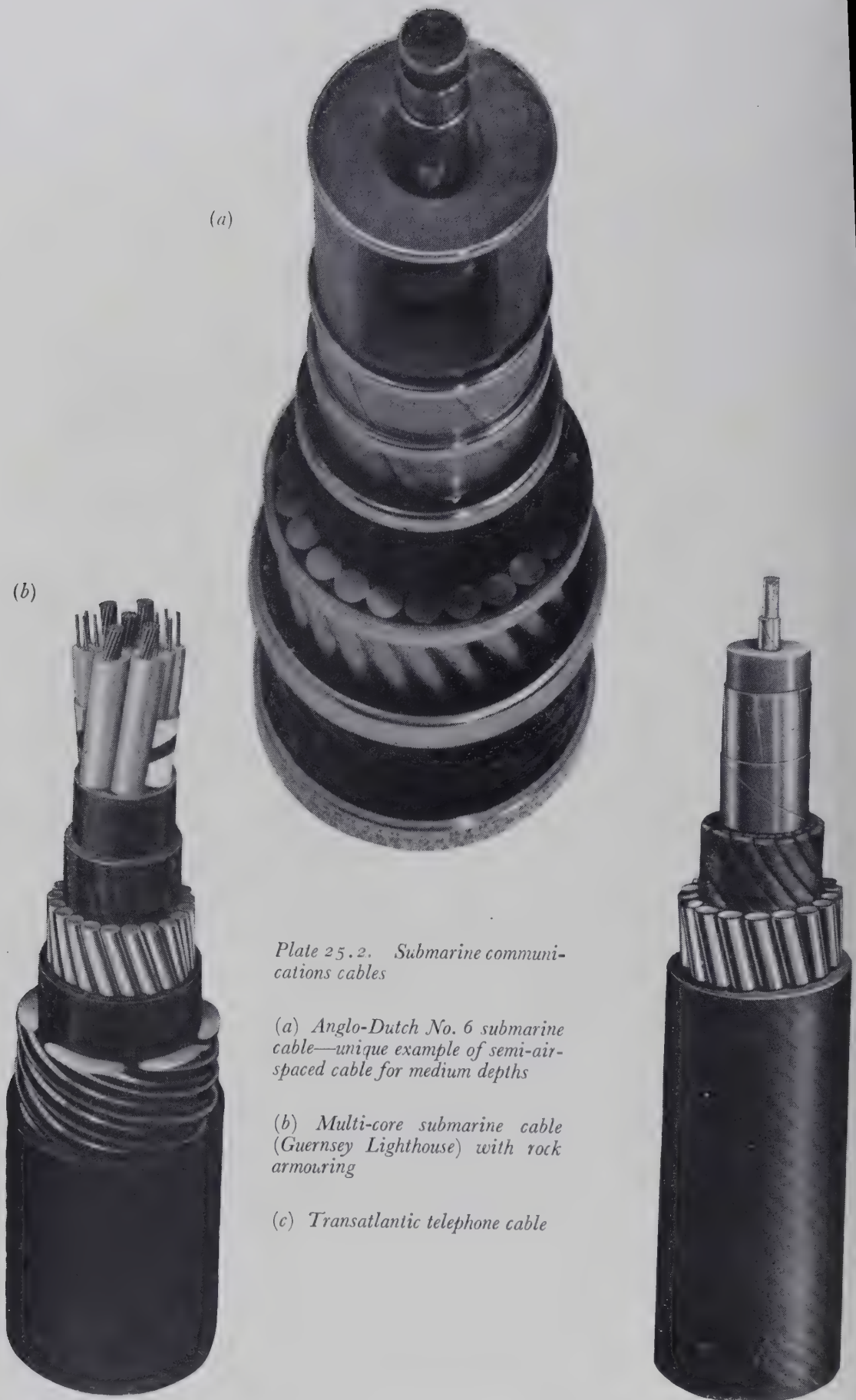


Plate 25.1. Radio frequency cables

- (a) Solid polythene lead-sheathed coaxial R. F. cable
- (b) Semi-airspaced flexible coaxial R.F. cable (polythene thread-and-tube insulation, copper wire braid and p.v.c. sheath)
- (c) Helical membrane cable (polythene helical tape insulation, aluminium sheath and p.v.c. jacket)
- (d) Cellular-polythene insulated flexible coaxial R.F. cable (copper wire braid and p.v.c. sheath)



(a)

(b)

Plate 25.2. Submarine communications cables

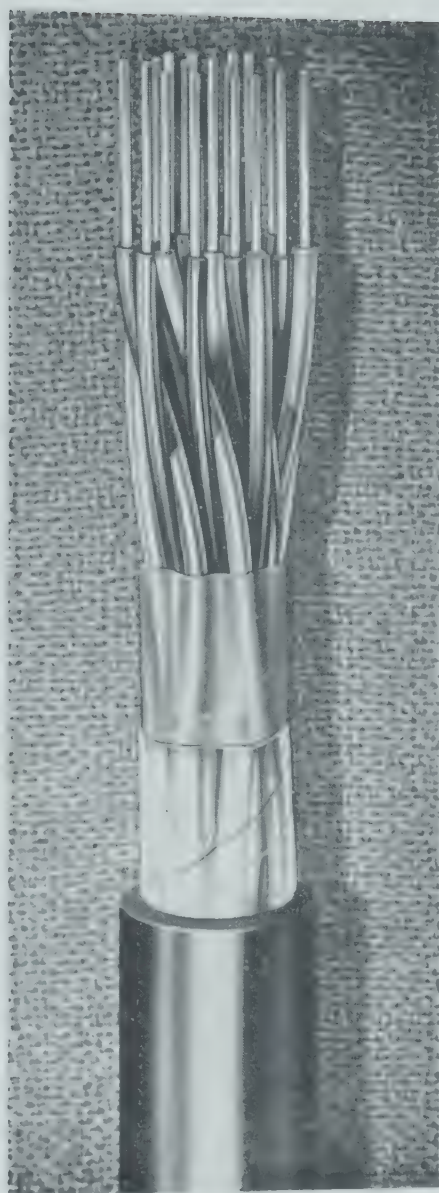
(a) Anglo-Dutch No. 6 submarine cable—unique example of semi-air-spaced cable for medium depths

(b) Multi-core submarine cable (Guernsey Lighthouse) with rock armouring

(c) Transatlantic telephone cable



(a)



(b)

Plate 25.3. Line communications cable for land use

(a) 7-quad 25 lb polythene-insulated, polythene-sheathed cable for 48-channel carrier working

(b) 10-pair 10 lb polythene-insulated, polythene-sheathed "subscribers" cable



(a)



(b)



(c)

Plate 25.4. Broadcast relay cables

- (a) *Polythene-insulated twin transmission line*
- (b) *Double-quad cable for audio working*
- (c) *Screened quad cable for television distribution*



Plate 25.5. Power cable : 11 kV 3-phase polythene-insulated, steel wire armoured cable

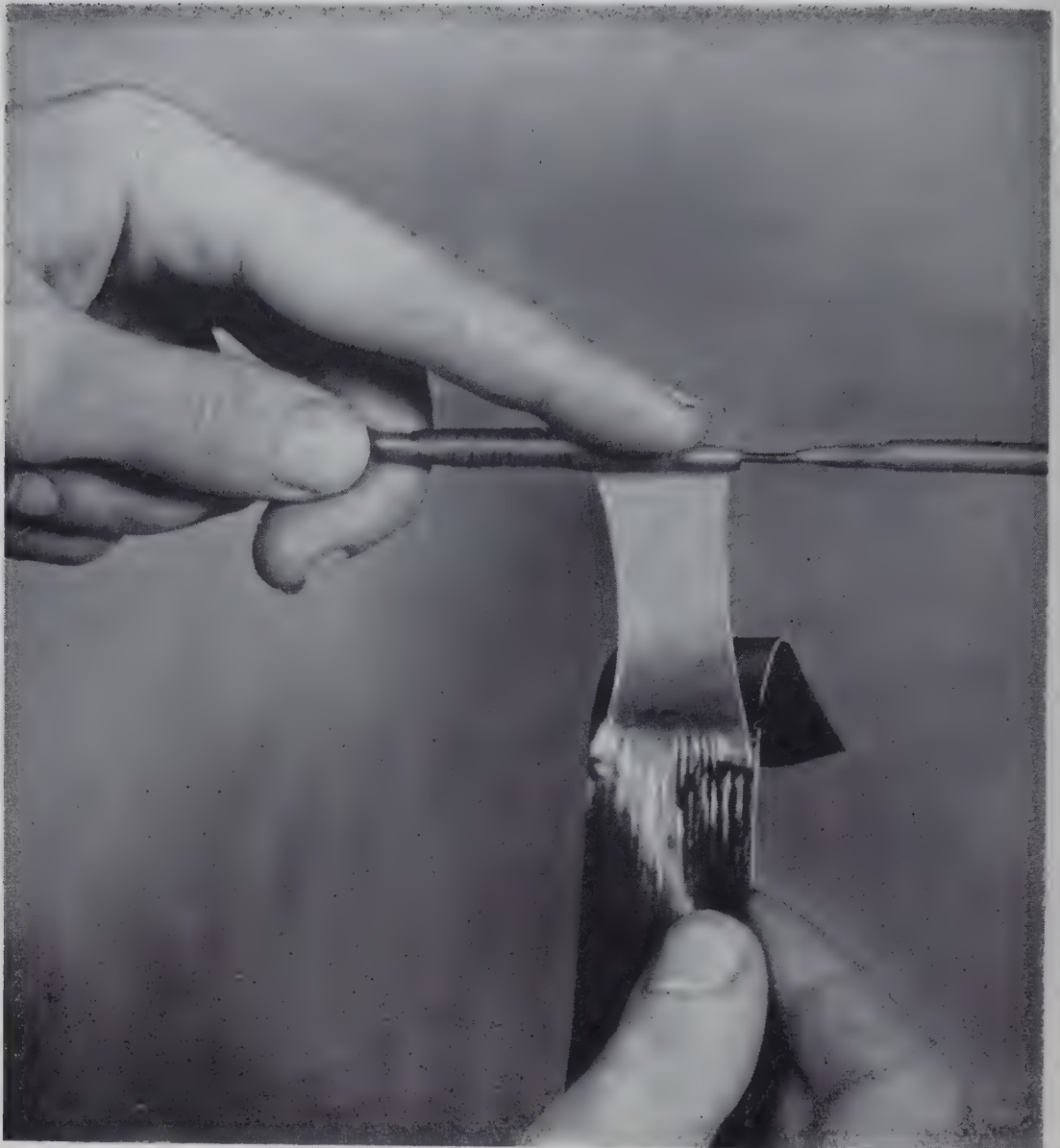


Plate 25.6. Applying self-adhesive jointing tape to a polythene cable joint



Plate 25.7. A polythene moulded insulator used to make a watertight termination for a coaxial cable feeding an open wire line and broadcasting transmitter aerial. (Courtesy Marconi's Wireless Telegraph Co. Ltd.)



Plate 25.8. Part of an aerial-mounting insulator for an aircraft transmitter-receiver. (Courtesy Ministry of Supply)

in U.S.A. when lead was in short supply and is an extension of an earlier design known as Alpeth in which the screen consisted of a longitudinal, corrugated aluminium tape overlapped at the seam and flooded with compound. Over the compound was an extrusion of polythene. In the later design aterne-plated corrugated steel tape was added over the aluminium, the overlapping seam of the steel being soldered together by induction heating. Compound was applied over the steel tape and a polythene sheath extruded overall. The object of the compound was to prevent the entry of moisture into the interior of the cable which contained paper insulated cores. A still later version known as P.A.S.P. is identical with Stalpeth but has a polythene sheath immediately under the aluminium screen.

The low coefficient of friction makes polythene sheathed cables well-suited to duct installations.

Broadcast relay cable

In this country as elsewhere the system which uses a wired circuit to transmit audio-programmes to subscribers constitutes an important usage of cable, and in this country the use of polythene for insulating such cables is general. Such cables are made with core wall thicknesses of about 18 mils with a 25 mil polythene sheath and are supplied in the form of single or double quads. Alternatively, a single-pair cable with two parallel wires and insulated in the form of a dumb-bell has been used. The performance of these cables is entirely satisfactory although in the past some adverse experience has been encountered due to the poor ultra-violet light ageing of natural polythene. Since that time a practice has grown of sheathing such cables with polythene loaded with carbon black.* Performance to date has been satisfactory, whilst laboratory tests indicate that the life of such material should be adequate for commercial installations. This usage has been extended to television programmes: in this case a screened version of quad cables is used.

CONTROL CABLES AND COVERED WIRES

Control cables

The use of plastics-insulated and sheathed cables to replace rubber has made some progress in spite of the conservatism of the users of such cable who have in general had satisfactory experience with the older designs. Their use is best justified in cases where the cable has to be operated in hazardous conditions, as for instance in damp situations and in cases where the cables are exposed to sunlight or to contact with oil or other contaminants. The bright easily-identified colours which can be given to polythene cores are valuable in these applications.

Covered wires

The use of polythene in such cases are in general subject only to two disabilities, namely the inflammability of polythene, and more particularly its liability to drip when burning, and also its poor resistance to

* See Chapter 6

deformation at very high temperatures. The former can be overcome by the use of flame retardant compounds. In certain cases the resistance to deformation has been improved by providing an overall sheath of which assists in avoiding the effect of local pressure at the point of stress which might otherwise cause trouble.

POWER CABLES

Polythene-insulated p.v.c.-sheathed cables to B.S.1557 have established themselves as an accepted design for electrical wiring cable for domestic and factory use.

Polythene-insulated cables have been used in this country as distribution cables only to a limited extent. In America there have been a number of new building estates where polythene distribution cables have been adopted. The lightness of the cable together with the lack of need for a water tight sheath can lead to certain savings in the cost of installation. One problem which has placed difficulties in the way of their wider use is that of combining this type of cable with the orthodox form of impregnated-paper lead-sheathed cable. It is difficult to provide a joint between the two cables which satisfies the full requirements of both.

In the field of high-voltage feeders again the adoption of polythene has been very slow indeed although initially there was a very great interest because of the attractive electrical characteristics of polythene. It is true to say that many of the companies which have explored the use have found the development most disappointing. By comparison with some other materials, polythene has poor resistance to ionic bombardment in gaseous discharges. There are two important problems encountered in the use of polythene. In the first place there is the difficulty of eliminating cavities of small dimensions caused by the high thermal contraction of the polythene when it is extruded, and incidentally, of maintaining the absence of spaces between the conductor and insulation when the cable is subjected in service to the thermal cycles caused by load current.* Secondly the limited overload capacity of these cables: this latter point arises from the fact that cables may have to withstand short periods of short-circuit due to faults in the system. Since such a fault may occur when the cable is fully loaded to its maximum temperature of say 60°, the margin between this temperature and the melting point itself of polythene is not large. The short-circuit rating of polythene cables is about 85 % of the rating of paper-lead cable as accepted at the present time. On the other hand the two attractive features of polythene cable, namely their light weight and their immunity from the hazards of moisture have led to continued interest in their use and today in many systems there will be found cases of high-voltage feeders for aerial and for submarine use. In this country this usage has been limited to voltages of 11 kV. three phase. In other parts of the

* See Chapter 16

CABLES AND OTHER DIELECTRIC APPLICATIONS

world the highest voltage that has been used has been somewhat higher, in America to about 15 kV. and on the Continent to 33 kV. In America there has been considerable usage of such cable for series circuits of lighting cable and also for special installations such as chemical works where corrosion conditions make the use of lead-sheathed cable very hazardous and for river crossings usually associated with overhead lines.

INSULATORS FOR HIGH VOLTAGES

The high resistivity and high breakdown strength of polythene make it very suitable for the construction of, for example, stand-off insulators.

Aerial lead-in mouldings for aircraft are conveniently constructed in polythene and it is also used for making shrouded connectors for Post Office telephone transmitter switchboards, and for the construction of electrode holders on spectrographs. Other applications include sleeving for the insulation of wires. Tool handles are often covered in polythene, for example pliers intended for general electrical work and cutters used by fire brigades for emergency severing of high tension cables. Another interesting application is the use of polythene tube for conveying cooling water to transmitter valves. These examples incidentally illustrate different methods of fabricating polythene and include moulding, polythene extrusion, and in the case of the tool handle application, dip coating.

LOW LOSS DIELECTRIC FOR HIGH FREQUENCY APPLICATIONS

It is a logical development from the use of polythene as the dielectric in cables for high frequencies to use the material as the insulant in coaxial connectors for such cables. This is sometimes done by the use of moulded inserts in a demountable type of connector and in other cases the cable end and associated metal fittings are integrally moulded to form a water tight plug or socket.

This last method illustrates the use of the high expansion co-efficient of polythene as on cooling after the injection moulding process the polythene shrinks down on to the p.v.c. jacket of the cable, ensuring a watertight seal.

In addition to the use of polythene at the equipment, as described above, the material is also of use at the aerial in the form of dipole mouldings as, for example, in certain radar installations. In the construction of general circuit components polythene is used for coil formers and, for example, in constructing sleeves for certain types of trimmer capacitor.

In the medical field "mushroom" shaped polythene mouldings are used to space radiotherapy electrodes at the correct distance from the patient.

At higher frequencies polythene is used in connection with microwave transmission. Polythene has been used for the construction of a Fresnel plate for focusing a beam of microwaves, and has also been considered for such uses as dielectric wave guides, for transparent windows in con-

ventional wave guides, and as a coating on surface wave transmission lines.

LOW VOLTAGE APPLICATIONS WHERE HIGH RESISTIVITY IS IMPORTANT

One such application is in the construction of antistatic aerials. Trouble was often experienced particularly on aircraft when bare metal aerials were used, due to electrical noise generated by charged particles in the atmosphere contacting the aerial. Covering the aerial with polythene is a way of avoiding such unwanted noise.

An illustration of the high surface resistance of polythene is given by the tendency for the surface of freshly-rolled polythene film to collect dust from the atmosphere; the surface becomes electrostatically charged and hence attracts the dust particles. In most cases a nuisance, this phenomenon has been put to good use by employing polythene film in air-conditioning plant dust filters.

Another interesting effect of the very high surface resistivity of polythene is the electrical noise generated in polythene-insulated coaxial cables when such cables are flexed or mechanically handled. This "microphony" is due to a tribo-electric phenomenon. When one conductor of the cable breaks contact locally with the polythene surface electrons are left behind on the polythene, and because of the high resistivity of the surface they do not leak away. The result is that small currents flow in the external circuit, and such currents are highly undesirable where, for example, the measurement of small ionization currents is being attempted. It is well known that this microphony can be very largely overcome by applying over the polythene surface a film of conducting material and cables with this feature are commercially available as "non-microphonic" types. However, the tribo-electric noise produced in untreated cables has recently been turned to advantage and has been suggested for use in a burglar alarm. This is done by surrounding the area to be protected by a polythene insulated cable and connecting it to a sensitive detector of small voltages. Any mechanical disturbance of the cable sounds the alarm.

FILM APPLICATIONS

E. D. FULLER, W. E. HENDERSON

AND P. H. LINDENMEYER

POLYTHENE film was first produced commercially as blown tubing in 1945. One of the first applications in the U.S.A. was the military use of seamless tubular rifle covers, where the low moisture permeability, high durability, and superior low temperature flexibility of this new film were employed to good advantage. When polythene became available for peace-time uses, there began a series of commercial discoveries of applications for which polythene film is suited. This market development still continues at a rather remarkable rate, and has been largely based upon sound applications of the unique combination of properties which characterize polythene film.

However, polythene is not a cure-all, and there have been misapplications. The primary purpose of this chapter is to present an over-all picture of both good and bad characteristics of polythene film, especially as they relate to various practical applications.

For the first several years of commercial development of polythene film, it was possible to satisfy most of the recognized use requirements to a reasonable degree with a single type of film. This situation can be traced to several factors. First of all, the supply of polythene was limited, so that there was no great pressure on the film manufacturers to develop new market outlets. Secondly, the extent to which the properties of polythene film may be modified was not realized for some time and thus the possibility of fitting this film to certain uses was not known. In addition, the lack of availability of sufficient polythene film to meet the demand inevitably weakened the normal bargaining power of the customer in seeking improved materials to fit his particular need. General purpose polythene films were employed, with a reasonable degree of satisfaction, in many applications where special types are indicated today.

The above situation no longer exists, nor is it likely to exist again. The increasing supply of polythene and the consequent availability of polythene film, the increasing awareness in the trade of the possibility of altering film properties to fit particular applications, and current and future advances in technology may all be expected to result in greatly increased complexity in the manufacture and marketing of polythene film.

We will discuss properties characterizing polythene films in general, specific requirements for an ideal film for some typical applications,

and the extent to which the properties of polythene film can be varied to fit those requirements.

Polythene film is produced by melt extrusion through suitable dies. Variation in the conditions of this process can markedly affect the properties of the resulting films. The high quality of film which is available today did not just happen, but is the result of extensive research and development.

PROPERTIES OF POLYTHENE FILM

General characteristics

Polythene can be melt extruded as a thin flexible film without the aid of any plasticizer, lubricant or stabilizer. This fact, together with the inert nature of polythene, results in films which are: (1) substantially colourless, tasteless, and odourless; (2) free from any toxic or objectionable ingredient; (3) unaffected by moisture, soil, and most common foods and chemicals; (4) not subject to embrittlement by plasticizer loss; (5) insoluble in all known solvents at room temperature. The inertness of polythene film is advantageous in food packaging and other packaging applications, in chemical packaging, in permanent building uses, and in most other end uses. In addition, the practically indefinite shelf life of the film, without discolouration or loss of toughness under ordinary warehouse conditions, helps to simplify handling, converting and distribution problems.

Polythene has the lowest density of all commercially available film-forming polymers. This property results in very high covering power per pound of material (30,000 sq. in./lb./1 mil thick), which combined with the relatively low cost per pound of polythene to give polythene film an exceptionally low cost per unit area. Light weight is also a distinct advantage in some applications where ease of handling is an important factor.

Polythene film is available in thicknesses ranging from less than 1 mil up to 20 mils in continuous lengths, as either sheeting or seamless tubing in widths up to sixteen feet, and as centrefolded sheeting in widths up to thirty-two feet. Rolls of gusseted tubing are also available.

Polythene film can be briefly described as an inert, flexible, low cost, durable, non-tacky, readily heat sealable film, having relatively low moisture permeability. It is usually semi-transparent, but can be made almost optically clear. It remains tough and tear resistant at food freezer temperatures, and even down to about -70°C . Its flexibility and resistance to tearing are not affected by atmospheric humidity.

Structural variations

Thus far, we have discussed only general properties which are common to all polythene films. When these properties are studied quantitatively, marked differences are observed from one film to another. These variations are great enough to render some polythene films suitable for a

given application where other polythene films would be entirely unsuitable. For example, the exacting requirements for a high altitude balloon film can only be met by careful selection of polythene resin and rigid control of extrusion conditions. Most polythene films would be entirely unsuitable for this application. One could very easily use for packaging dry goods a type of film which would be entirely unsatisfactory for the packaging of heavy items, such as apples, potatoes, etc. Some of the properties which differ markedly from film to film are impact resistance, stiffness, tear strength, and resistance to environmental stress cracking.*

Structural factors which account for the above property variations include: (1) molecular weight; (2) molecular structure; (3) crystallinity; (4) extent and type of orientation. The molecular weight and molecular structure are determined by the conditions under which the polythene resin was made, whereas orientation is almost entirely determined by the extrusion conditions. Crystallinity is primarily a function of molecular structure, but may be affected somewhat by extrusion conditions. The relation of these factors to the physical properties of polythene resins is discussed in other chapters. The orientation of the molecules, crystallites, or larger structural units in the film is one of the most important factors in determining the physical properties of the film. This orientation is extremely sensitive to conditions of extrusion.

Mechanical properties

Table 26.1 shows some mechanical properties of three types of polythene film. The first type is slot extruded film which has been drawn in only one direction. The second is a typical blown tubular film which has been biaxially oriented. The third film is a premium material manufactured specifically for the fabrication of high altitude balloons and has exceptional mechanical properties. These data are given to illustrate the range of variation of mechanical properties in existing commercial films.

It can be seen from the data in Table 26.1 that tensile strength and elongation vary considerably from one film to another. For most ordinary film applications, the extent of variation of these properties in current polythene films is seldom commercially important. However, in those applications which happen to demand excellent tensile properties, these characteristics can obviously determine the thickness of film required for a given application. In such cases tensile properties can certainly affect the economics of the application.

The resistance of a film to impact is a vitally important property in some applications. This property varies widely among commercial polythene films. No standard methods of measurement of impact resistance of thin films have been adopted. Probably the simplest test is to measure the minimum height from which a given falling ball will just rupture the film. Measurements of this kind show that impact

* See Chapter 10.

POLYTHENE

Table 26.1. MECHANICAL PROPERTIES OF POLYTHENE FILM

		Balloon film	Blown tubular film	Slot- extruded sheet
Tensile strength (lb./sq. in.)	M.D. T.D.	3,450 3,630	2,700 1,600	3,000 1,500
Elongation (per cent)	M.D. T.D.	570 825	250 400	130 560
Tear strength (grams/mil)	M.D. T.D.	110 180	210 140	220 110
Impact height (feet)		6+	3-4	1-2

strength is affected by the molecular weight, by the degree of crystallinity and by the orientation induced by extrusion.

Another important mechanical property is the resistance of polythene film to tearing. It is this property which permits produce bags to be perforated for proper ventilation, without any significant loss of durability. Two standard methods are available for measuring tear strength. One of these (ASTM D-1004-49T) measures the force necessary to initiate a tear, and the other (ASTM D-689-44) measures the force required to propagate an initiated tear. Neither of these methods is considered very satisfactory in evaluating the quality of polythene films, since there has been considerable difficulty in correlating test values with use performance. However, resistance to tearing is an important physical property which differs markedly from one film to another, even though a satisfactory quantitative measurement is not yet available.

Still another important mechanical property is the stiffness of polythene film. A stiff film may be advantageous to the converter in the operation of certain types of automatic bag making machines, whereas the more common soft, flexible film is fully accepted in many applications. One of the simplest measurements of stiffness is the modulus of elasticity in tension. This modulus is defined as the slope of the stress-strain curve, and is generally taken at low elongations, where the stress-strain

Table 26.2 GAS AND WATER VAPOUR TRANSMISSION RATES

Water vapour	1.4	(1) Water vapour transmission rate is reported in grams/100 square inches/24 hours/mil, and is measured at 90% relative humidity and at 100°F.
Nitrogen	180	
Oxygen	550	(2) Gas transmission is reported in cc/100 square inches/24 hours/mil, and is measured at 77°F with a pressure differential of 725 mm of mercury across the film. Data are reduced to standard temperature and pressure.
Helium	1,225	
Hydrogen	1,960	
Carbon dioxide	2,900	
Sulphur dioxide	6,200	
Ethylene oxide	29,300	
Methyl bromide	79,100	

FILM APPLICATIONS

curve is essentially linear. Unfortunately, most polythene films show a distinct curvature in the stress-strain relation, even at very low elongations. This requires a somewhat arbitrary definition of the modulus, depending upon the method by which it was measured. Stiffness of polythene depends largely upon crystallinity, with the more crystalline material being stiffer.

Permeability properties

For most applications polythene film represents a very good moisture vapour barrier. Its oxygen and carbon dioxide transmission rates are

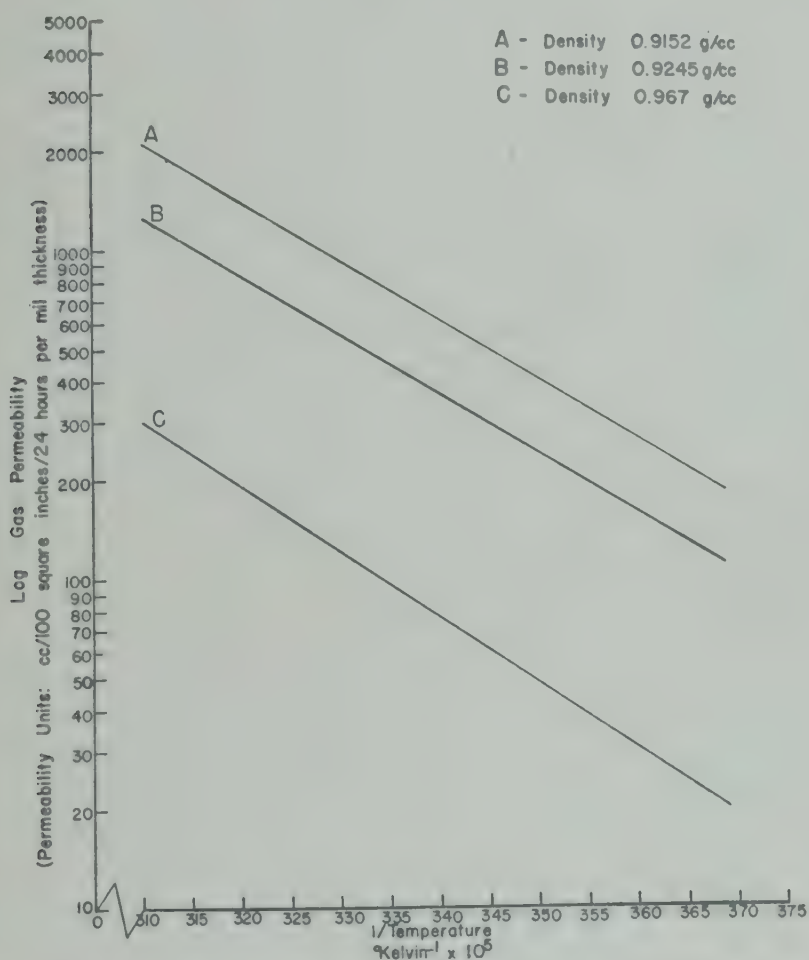


Fig. 26.1. Temperature dependence of oxygen permeability for polythene films of different densities. The log of oxygen permeability is plotted against the reciprocal temperature

relatively high. In Table 26.2 are listed transmission rates for moisture vapour, oxygen, carbon dioxide and other gases. These figures represent average values for typical polythene films. A given film may have a somewhat higher or lower transmission rate.

Two factors are known to have important effects on the permeability of polythene film: the degree of crystallinity; and the temperature. The greater the degree of crystallinity, the lower will be the transmission rate,

POLYTHENE

although the relationship is not linear. The transmission rate varies exponentially with the reciprocal of absolute temperature. In Fig. 26.2 the log of oxygen permeability is plotted against reciprocal temperature for polythene films having varying degrees of crystallinity, as indicated by density. This figure shows the marked decrease in oxygen transmission with decreasing temperature. This is commercially important since a film may have what appears to be an unacceptably high oxygen transmission at room temperature, but it may be sufficiently low at frozen food temperatures to be acceptable. A similar relation exists between moisture vapour transmission and temperature (Fig. 26.2).

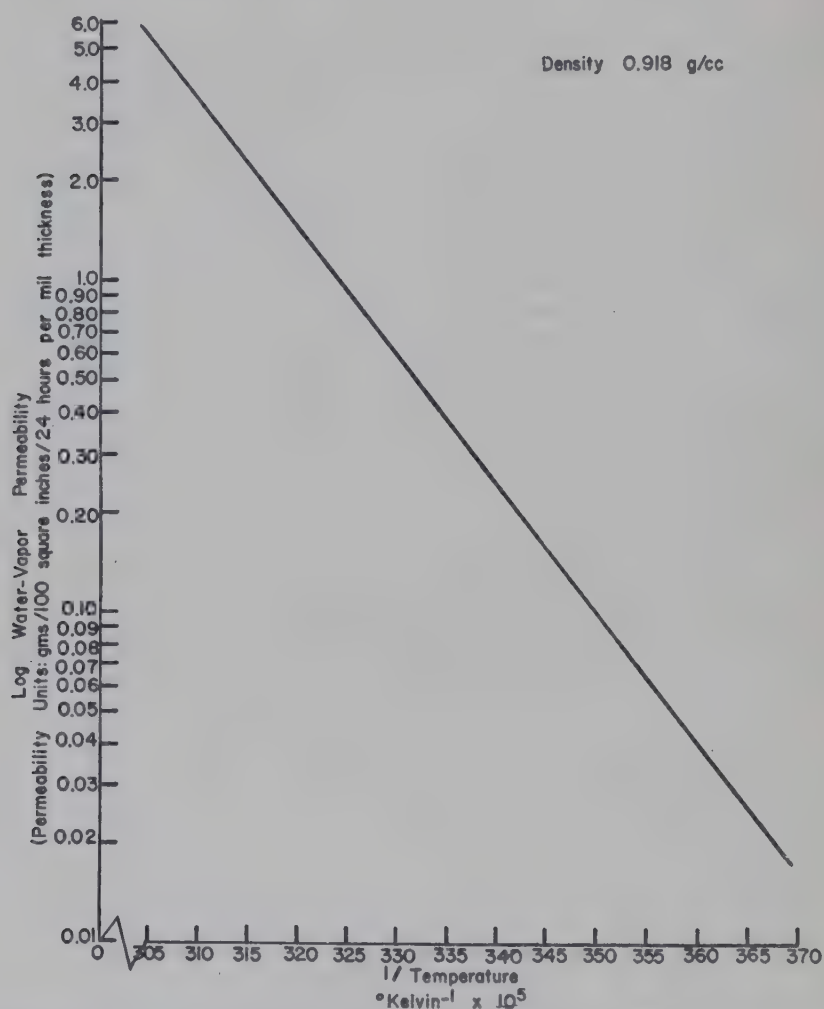


Fig. 26.2. Temperature dependence of water vapour permeability for polythene film. The log of water vapour permeability is plotted against the reciprocal temperature

The relation of permeability properties to the thickness of polythene film is of considerable importance in film applications. In thin films (up to approximately 10 mils), the rate of transmission of water vapour, oxygen and most permanent gases varies inversely with thickness. Exceptions to this rule have been found in material of greater thickness and in the permeability to some liquids and vapours.

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Table 26.3. TRANSMISSION OF ESSENTIAL OILS THROUGH POLYTHENE FILM

Oils	Grams per 100 sq. in. transmitted by 2-mil film in 24 hrs.	Oils	Grams per 100 sq. in. transmitted by 2-mil film in 24 hrs.
Vanillin	0.018	Lemon oil	14.241
Methyl salicylate	1.150	Orange oil	14.033
Coriander oil	0.879	Grapefruit oil	16.756
Petit grain	0.606	Cassia oil	0.262
Nutmeg oil	7.470	Geraniol	0.168
		Geranium oil	0.423

Polythene film is generally quite permeable to all organic vapours, essential oils and related materials, with the possible exception of highly polar ones (e.g., alkyl amines). The transmission of various essential oils through polythene film is shown in Table 26.3.

It is not always possible to judge the suitability of film in a given application on the basis of measured transmission rates. For example, the permeability of polythene film to sulphur dioxide and methyl bromide is quite high. Yet, polythene film has proved very successful in fumigation applications using methyl bromide, and has been used successfully in packaging silverware and other silver articles to prevent tarnishing. Apparently, all that is required in these applications is to prevent the free exchange of air, transmission rates being relatively unimportant under these conditions.

Optical properties

Polythene film is quite transparent to radiation in the visible and infra-red regions, with the exception of certain specific absorption bands. Transmission in the ultraviolet falls off rapidly below 300 millimicrons. The data in Table 26.4 indicate that, while polythene film is not quite so transparent to the sun's radiant energy in the visible region as ordinary window glass, it is more transparent in the ultra-violet and the infra-red regions.

Table 26.4. PERCENTAGE OF SUN'S RADIANT ENERGY TRANSMITTED

Spectral range (Millimicrons)	Polythene		Window glass
	8 mil	4 mil	double strength
Ultra-violet (200-400)	60%	70%	40%
Visible (400-720)	75%	83%	90%
Infra-red (720-2,500)	88%	90%	80%

The more common commercially available polythene films are what hazy, are only partially transparent, and often lack the high clarity of some other packaging films. Trade demands for clear polythene films are increasing, and have already led to the development of films with improved clarity and gloss.

Two distinct surface phenomena are largely responsible for the imperfections in thin polythene films. We will refer to these phenomena as "haze" and "grain", since these terms are becoming accepted in the polythene film trade. In actual fact, an inconsistency should be mentioned. "Haze" is really an optical effect *resulting* from one type of surface imperfection, whereas "grain" describes another type of surface condition which *causes* another optical effect.

Haze is normally understood to refer to scattered light. An instrument in use for determining haze of polythene and similar films is the integrating-sphere hazemeter. This device consists of a reflecting inner spherical surface, which is equipped with a photocell, mounted 90° to the path of a beam of light which passes through a pair of opposing holes in the sphere. The quantity measured is essentially the total percentage of transmitted light which is scattered far enough from the beam to reach the exit hole, when a film is stretched over the inlet hole.

It is not difficult to verify the fact that most of the haze from typical thin polythene films results from a surface condition. If a film is sandwiched between two glass plates wetted with an inert liquid having the same refractive index as polythene, nearly all of the haze disappears. The contribution of internal irregularities would, of course, become a major factor in thicker sheets.

It is generally believed that the fine-scale surface roughness which causes haze is due to the spherulitic structure of polythene. At a certain rate, haze can be reduced substantially by shock cooling the molten film, which appears to reduce the average size of the spherulites.¹

Most polythene films also show a grainy texture, which is referred to in the trade simply as "grain". This type of roughness is on a much larger scale, such that the individual hills and valleys are visible with little or no magnification. It appears that the pattern must consist of relatively regular, shallow, lens-like components, which give rise to angular refractions of light rays, as opposed to the random scatter produced by the fine-scale pattern which is superimposed on the grain.

Grain is indicated numerically through measurement of the optical effect which it produces. One simple test apparatus consists of a constantly illuminated optometrist's chart, mounted behind the film. The maximum separation of the chart and film which permits reading of a predetermined line of type can be used as an arbitrary "transparency rating". This test provides a rough indication of the extent of the angular refractions mentioned above.

Grain seems to be caused, partially at least, by a lack of homogeneity of the polymer. At any rate, it can be reduced somewhat by hot processing, in a Banbury mixer or similar device.

It is important to remember that the hazemeter measures forward scatter, and this does not necessarily correlate with visual transparency (i.e., distinctness of transmitted image). Our purpose is to show the practical importance of each of these effects.

Transparency is of direct importance only in applications which involve vision through the film of objects which are *not* in direct contact with the film. Examples include storm windows and windows in the tops of cardboard cake boxes. Visibility of objects in direct contact with the film is not materially affected by grain.

Haze is detrimental to appearance in most packaging applications. It should be pointed out, incidentally, that it would be more direct to measure *backward* scatter (i.e., diffuse reflection), since one usually has the light source on the same side of a packaging film as the observer. The hazemeter provides some indication of the milky greying effect which is observed when a film is held over a black or coloured background in bright sunlight (this effect causes ripe tomatoes in a window carton to appear to take on a dusty, pastel shade) but diffuse reflection measurements provide a more reliable indication in the case of relatively clear films.

Surface gloss may be dependent upon one or both of the above types of surface roughness, depending upon one's definition of "gloss". If gloss is taken to be a specular reflection at 45° , as measured through a coarse receptor slit (poor resolution), it is found to correlate with haze. That is, the small-angle distortions caused by grain (at least in the case of reasonably transparent films) are within the slit width. This type of gloss can be called contrast gloss. If specular reflection at 45° is measured through a fine receptor slit (good resolution), it is found to be affected by grain, as well as by the fine-scale roughness which causes haze. This type of gloss can be called "distinctness-of-reflected-image" gloss.

The importance of gloss arises partly because of its value in attracting attention, and the reflection of distinct images of light sources is certainly a factor. Thus, grain is of some importance even in direct-wrap applications, due to diffusion of *reflected* images.

Printability

The soft, waxy nature of polythene film, which is desirable for many applications, has proved to present a very difficult problem in printing. Since 1945, when the first commercial polythene film was produced, considerable effort has been directed toward attaining permanent ink adhesion, through both modification of film properties and improvement of printing inks and printing techniques. Today, specially processed printable films are being manufactured by several film producers. These films have one or more surfaces which permit permanent bonding of ink to the film. Thus, it is now possible to obtain excellent adhesion on properly treated polythene film with flexographic, letterpress, and roto-gravure inks without the use of any anchor coatings, as were formerly recommended. Flexographic inks are available from commercial ink

manufacturers which have high gloss, hiding power, good adhesion, and rapid drying characteristics.

Sealability

Polythene film is probably the easiest thermoplastic film to heat seal. A wide variety of commercial sealing devices have been developed and modified for fabricating polythene. These include high speed automatic, hand-fed semi-automatic, and manually operated devices. The bar sealer is the most commonly used sealing technique. However, heat sealing may be effected by any suitable device which supplies sufficient heat to the film while it is held in intimate contact. This may be accomplished by means of a hot wire, a bar heated by electrical impedance, a heated rotating band, or a flame.

One of the largest uses for polythene film is the fabrication of bags for various applications. The majority of polythene bags are produced by machines designed especially for packaging converters. These machines will produce bags of predetermined size from rolls of printed or unprinted polythene film or tubing. Commercially obtainable machines produce from 40 to 120 bags per minute, depending upon the size of the machine. Multiple webs may be run to further increase the output per machine. Most polythene bags are produced in the thickness range from $\frac{1}{2}$ to 4 mils. An automatic bag machine has been developed for producing a bag with a curved end-seal, for use in packaging poultry and other items which require a form-fitting bag.

Larger bags can be made on existing commercial machines by using gusseted tubing. When gusseted or flat bags are produced from single thickness film, a forming plate is used to obtain a centre seam. The bottom seal is generally produced by the straight bar method, immediately prior to the cutting and stacking operations.

The commercially available bag-making machines may be equipped with devices for automatically perforating the bags for ventilation.

Bags are also produced by hand-feeding precut lengths of tubing between heated jaws, which may be foot operated. These machines are capable of up to 40 cycles per minute, and are generally used where quantities do not warrant automatic or semi-automatic equipment. Wide bags and flat bottom liners are generally produced in this manner. Special equipment is available for round bottom and other shapes.

The ideal adhesive for polythene has not yet been found. To date, adhesives have not been used for bag fabrication; however, adhesives satisfactory for lamination work and spot gluing are available. These are generally of the latex type and require the escape of water or solvent for setting. Combinations of heat sealing and spot gluing are used for producing duplex bags (double wall bags, with one layer being polythene film, and the second layer being of paper or fabric).

Slip and blocking

The terms "slip" and "blocking", which are commonly used in the film trade, may require definitions. For our purposes, we will consider

"slip" to relate to the resistance of the film to a sliding action over another film surface or over a metal surface. A film with good slip will slide smoothly and easily. "Blocking", on the other hand, is the resistance of two films to separation by a perpendicular or peeling force. These two film properties are generally very closely related, since they both depend upon surface forces. They are not identical, however, and polythene films exist which have very good slip, but which tend to block severely.

It should be pointed out that slip and blocking problems in polythene films are much less severe than for many other films. Nevertheless, poor slip characteristics of polythene films have caused serious concern to users of automatic bag making machines. Blocking in polythene films can become a critical problem, especially when filling bags with light articles (e.g., marshmallows). No standard methods for the quantitative measurements of these two properties have been published, although various practical tests are in use. Some of these tests use a sensitive spring balance for the measurement of sliding frictional force in determining slip, and peeling force in determining blocking.

APPLICATIONS

Food packaging and preservation

The requirements of a film for the successful packaging of fresh fruits and vegetables are: (1) low moisture vapour transmission; (2) easy exchange of oxygen and carbon dioxide; (3) toughness and flexibility at all storage temperatures; (4) pleasing appearance, freedom from odour and flavour and non-toxicity. Polythene film meets all of these requirements remarkably well.

At room temperature, even the relatively high oxygen and carbon dioxide transmissions of polythene film are not sufficiently high to prevent spoilage, and perforation is necessary to assure adequate ventilation. It is somewhat surprising to note that it is possible to perforate polythene bags with a number of $\frac{1}{8}$ – $\frac{1}{4}$ in. diameter holes, in order to permit sufficient oxygen and carbon dioxide interchange, and still to have a bag which will retain sufficient moisture vapour to prevent the produce from drying out.

The tear strength and durability of polythene film are important in preventing the perforations from tearing. Extensive testing of the resistance of produce bags to tumbling, dropping, and vibrating have shown no important differences in durability characteristics between bags which have been perforated, and the unperforated type. In the packaging of heavy fruit and vegetables, the resistance of the film to impact is important. It is common practice to fill bags with potatoes, turnips, etc., by dropping the produce through a loading hopper into the bags. Failures in impact have occurred occasionally in these uses, both in this filling operation and during rough handling of the filled bags. Such failures usually appear as sharp splits, often along fold lines. Fortunately, films can be extruded in such a manner that they will

withstand such treatment. Proper control of impact strength is becoming increasingly important in the produce packaging field.

Polythene film is now extensively used in the prepackaging of fruits and vegetables. Large quantities of carrots are being packed in printed polythene bags at the grower level. The savings in labour that resulted from trimming the tops have more than paid for the bagging. The same practice is rapidly growing for beets, turnips, radishes, and other root crops. Apples, oranges, grapefruits, lemons, and onions are being prepackaged at the grower, terminal, and retail levels in polythene bags of sizes demanded by the housewives. The manufacture and re-use of polythene bags and bowl covers for the storage of foodstuffs in the household refrigerator are now familiar.

Polythene film is also used in packaging other food products such as cookies (biscuits), marshmallows, and other sweets. One important application is the packaging of frozen poultry in contour bottom bags. The first requirement in this application is that the film possess a sufficiently low moisture vapour transmission rate to prevent the development of "freezer burn" through local dehydration. Furthermore, it is essential that the film remain intact, through the whole chain of distribution, to the ultimate consumer. If the package punctures, splits, or opens at the seals because of low temperature conditions, contact with ice or ice crystals, or rough handling, the film is not performing its intended function. The great toughness and durability of polythene film under low temperature conditions insures good functional performance for all types of frozen poultry.

In the packaging of meats and poultry, high oxygen transmission is a disadvantage. Note, however, that oxygen transmission falls off sharply with temperature (Fig. 26.1), so that in the packaging of frozen meats and poultry, this is relatively less important.

Chemical packaging

This field of application in general makes use of the chemical inertness of polythene as well as its low moisture vapour transmission (MVTR) and toughness. The most common use is in the form of drum, carton, or bag liners. A fibre drum with a polythene drum liner has in many instances replaced returnable steel drums and thus saved much shipping cost. Such drum or bag combinations are being used for a variety of solid chemical powders or crystals and they reduce to a minimum such problems as contamination, caking and damaged containers. Polythene liners are often usable for aqueous solutions, emulsions, latices and similar chemical products. In all cases actual testing of the product in the package is recommended before attempted use. Polythene liners in drums, cartons and bags have found many uses for transporting fresh and frozen bulk food products and chemicals.

Packaging of dry goods, hardware, notions

The unequalled stability of polythene over a long period of display shelf-life is the primary reason for its acceptance in this field. Use



Plate 26.1. Polythene film is extensively used in the pre-packaging of fresh fruit and vegetables



Plate 26.2. Turkeys packed in polythene bags which are shrunk over the birds



Plate 26.3. The protective properties of polythene film are made use of in the packaging of dry goods



Plate 26.4. Polythene film is laid as a permanent moisture barrier under concrete



Plate 26.5. Polythene film being laid over fresh concrete. This technique permits slow curing for maximum strength



Plate 26.6. Large scale use of polythene film for curing concrete



Plate 26.7. A special type of film is used for high altitude research balloons



Plate 26,8. Crops can be treated with pesticide by sealing temporarily with polythene film



Plate 26.9. Fumigation of house is carried out after sealing with polythene film

FILM APPLICATIONS

made of the mechanical and moisture protection polythene affords, as well as the absence of migratable plasticizers or stabilizers, or of corrosive action on metal surfaces.

One important use is represented by small transparent polythene packages for nails, tacks, screws, etc., in hardware stores. Similarly many automotive and other mechanical parts are now protected by polythene film either singly, as repair kits, or as entire replacement units.

Bags made of polythene film have proven to be useful as merchandise containers for a host of items such as shirts, gloves, hand bags, sweaters and hosiery, to mention only a few. Toys, baby goods, marbles, sheets and pillowcases, blankets and thousands of other items are currently being packaged in polythene. Polythene bags have found wide use as effective containers for combination sale items of housewares and "notions," ranging from soap to beer cans.

Building materials

The low moisture vapour transmission of polythene film, coupled with its toughness, flexibility, durability, inertness and light weight has made it particularly desirable as a permanent moisture barrier in building construction.* Polythene film does not deteriorate appreciably in contact with soil, nor will long contact with air affect its properties, as long as it is not exposed to sunlight. It is used under slabs, footings and foundations as a permanent moisture barrier. It is also used as a lining for concrete forms and for covering fresh concrete. When used for this purpose, it permits easy removal of the forms and slow curing of the concrete for maximum strength. In addition, polythene film is suitable for use as a moisture-proof, dust-proof barrier in floors, sidewalls and ceilings. It is particularly valuable in the structural walls of shower stalls and bath areas, to prevent the transfer of moisture. Low cost, ease of handling, and superior mechanical properties make polythene film a desirable replacement for building paper in most applications.

The availability of very wide material (up to 32 feet) without seams has encouraged the use of polythene film as a moisture barrier in building.

SOME SPECIAL POLYTHENE FILMS

Shrinkable film

A type of polythene film is now commercially available which will shrink about 25-45% in each direction when it is suddenly heated to temperatures of 103-108°C. This material is non-toxic and has the excellent moisture-proofness, low temperature flexibility and all of the other general characteristics of polythene films as described previously. One interesting application for this film is the packaging of turkeys or other poultry for freezer storage. A dressed turkey is placed in a shrinkable polythene bag, the bag is evacuated and tied, and the entire package is immersed in a hot liquid. Since the film shrinks in both directions,

* Cf Chapter 28.

it draws down nicely around the legs, wings, and other irregular contours of the bird to form a protective skin. Such packages will not open during handling at freezer temperatures.

Elastic film

It is also possible to produce snug-fitting protective wrappers for poultry by stuffing the birds into bags which are smaller in circumference than the birds themselves. For the success of this application it is necessary to have a film which can be stretched considerably (40-100%) in the transverse direction, and which will show a large amount of elastic recovery upon being released. It is also necessary that the film should possess some elasticity in the machine direction, but this is seldom a limiting factor. Most polythene films can be stretched to a limited extent in the machine direction without necking down, and will show considerable elastic recovery upon release. However, when ordinary polythene films, as they are usually supplied today, are stretched to a considerable degree in the transverse direction, they neck down abruptly. As a result, most of the stretch occurs in these cold-drawn portions, and is largely inelastic. The disadvantage of this characteristic in attempting to produce a smooth undistorted wrapper is self-evident. (A polythene film is now commercially available which may be stretched up to 100% in either direction without necking down, and which will recover up to 80% of this elongation upon release. These packages can also claim the advantages of low temperature flexibility, low cost, moisture-proofness and the other general characteristics of ordinary polythene films.)

Balloon film

A special type of polythene is available for use in high altitude balloons intended for cosmic ray studies and similar purposes. This film has unusually high and well balanced tensile strengths, a consistently low embrittlement temperature, and an exceptionally low frequency of pinholes. Considerable amounts of this material have been successfully used in numerous high altitude balloon flights.

Outdoor applications

Polythene film is finding considerable success as a low cost roofing material for seed beds and greenhouses. It is not necessary to have an optically clear film for this application. Typical polythene films scatter and/or diffuse a significant proportion of the incident light, but this is not a disadvantage in this case. Very little of the incident light is reflected or absorbed.

Although polythene film is probably the most sunlight resistant of any of the low cost transparent films, when an ordinary polythene film is exposed to bright sunlight for several months, photochemical oxidation occurs. The film tends to become somewhat brittle and breaks with less elongation. This does not completely exclude the outdoor use of clear film. For example, it is quite satisfactory as an expendable covering for freight cars, greenhouses and for equipment stored outdoors.

in temperate climates. Polythene Greenhouses in Finland are reported to have a 3 years life. However, tropical sunlight will usually cause the film to deteriorate in less than a year.

Films are available which contain carbon black to render them opaque to the destructive radiation. Such films are in use as tarpaulins, in a special tensilized form as pipe-line wrapping tape, in irrigation tubing, as liners for irrigation ditches, etc. One of the most interesting applications now being developed is in the field of agricultural mulching. Black polythene film may be economically used as a ground cover in gardens, nurseries, or for any crop of relatively high value. It is superior as a moisture barrier to the papers which are sometimes used in this way and is permeable to oxygen. Many produce growers are interested in using black polythene film to conserve soil moisture and inhibit weeds.

Camelback backing film

Polythene film is employed in the rubber industry as a backing for rubber sheeting, to prevent sticking together on the roll. For this purpose, the film is embossed to permit easy stripping from the rubber. The principal requirement of such film is high tear resistance, so that it can be peeled off intact. It is usually coloured for identification purposes.

Miscellaneous

Ordinary polythene film will support combustion under some conditions. If a crumpled sheet of film is ignited, for example, it will not flash nor support a roaring fire, but will melt down in a pile and burn like a candle. For applications where even this degree of inflammability is undesirable, additives may be incorporated for flame retardency.

Polythene film has excellent characteristics as an electrical insulator, but a slight degradation during processing tends to impair these properties a little. Anti-oxidants may be used to prevent this degradation for the more demanding electrical applications.* Flame-retardant and electrical-grade films are not usually suitable for use in contact with foodstuffs. However, non-toxic anti-oxidants are also available.

Polythene film is also available in a wide range of colours and it may be embossed with various patterns. It is employed in marking tapes, pennants, tablecloths and other decorative applications.

FUTURE IMPROVEMENTS

It has been pointed out that some properties of polythene film may be varied over rather wide ranges, by means of alterations of the basic molecular structure and orientation of the film. We will mention here only certain effects which may have definite commercial importance.

New ethylene polymers are expected to become commercially available at a rapid rate in the near future. Definite progress in the science and technology of thin film extrusion has been made in recent years, and

* See Chapter 6

greater advances may reasonably be expected. In addition, a technique is now available for cross-linking the polymer after it has been extruded in thin film form, by high speed electron irradiation.

Some improvements in film properties may be expected only at the sacrifice of other properties, and will thus be built into specialized films.

Mechanical properties

Some very marked improvements in tensile strength may be expected. The principal advantage of this is self-evident. In those applications where tensile strength is a limiting factor, it will be possible to use thinner films. Higher tensile strengths may also be particularly advantageous for some specialized applications, such as tapes.

The trend toward thinner films is not always limited by tensile strength. Because of the limp, relatively rubbery character of most polythene films, they are rather difficult to reel, handle and process with automatic machinery in thicknesses less than one mil. Films may be expected which are stiffer and have greater dimensional stability. This may also have the effect of extending the range of types of converting equipment which may be used with polythene film.

Films may be expected with even better low temperature durability. This may be important in some military applications, particularly at very high altitudes. The low temperature durability of polythene is certainly adequate now for most ordinary uses.

Higher softening temperatures

Polythene films may be expected which will withstand boiling water or even steam sterilization without distortion. This should extend the utility of such films as drum liners and for other industrial purposes and should also permit the use of sterilizable packages.

Lower permeability

Polythene films will become available which have still lower moisture vapour permeabilities than present films, thus permitting the use of thinner films in cases where moisture permeability is the limiting factor.

Clear films

Last, but certainly not least, we may expect polythene films with greatly improved optical clarity, freedom from the usual milky haze and much higher gloss. Most of the more transparent polythene films which are commercially available today suffer from one or more of the following disadvantages: poor impact strength, poor sealability on high speed equipment and tackiness (which may be aggravated by a tendency to accumulate static electricity). Methods for preventing the occurrence of each of these defects are known and some of them are already in commercial use. The effect this may have in extending the application of polythene films, particularly in packaging, hardly needs elaboration.

REFERENCE

1. Eryant, W. M. D., *J. Polymer Sci.*, 2, 547 (1947).

CHAPTER 27

DOMESTIC, AGRICULTURAL AND INDUSTRIAL PIPING

W. L. THORNE

POLYTHENE pipe represents the first addition to the traditional range of water pipes for the last three decades. The normal materials used for this function are lead, copper, and galvanized iron. The use of copper for conveying water has existed from the earliest times, but it was not until the present century that it became available in the form of light gauge drawn piping. None of the traditional materials is ideally suitable and unless special precautions are taken all existing water pipes corrode when buried in the earth. Lead is the least corrodible of metal pipes but the risk in using it is serious in soft water areas. Polythene on the other hand, has a special claim for consideration in this field since it is free from the corrosive effect of both soils and water supplies. Despite these obvious advantages of polythene over traditional materials its application to water services began very slowly because it had to establish itself in the face of much prejudice and conservatism. Now that standards are established, giving the water engineer some guarantee of quality, polythene pipe is being used at an ever increasing rate. Some idea of this expansion can be gleaned from the fact that over 40,000,000 lb. weight of polythene (including scrap polythene) was converted into pipe in the U.S.A. in 1955.¹

HISTORY

Each traditional water pipe material has a sphere in which it gives a reasonably satisfactory service performance. The effect of the pipe material on the taste and odour of drinking water and the possibility of toxic hazard is a matter of prime importance. Many soft waters dissolve lead, and have therefore to be treated to prevent a toxic hazard, but there are still many private water supplies which are not treated, and the risk of toxicity in such cases is very real. A D.S.I.R. report² indicates that polythene does not affect the taste or odour of either untreated or treated drinking water, nor does polythene provide a toxic hazard.

Quite apart from the effect of the pipe material on the water, it is equally important that the pipe itself shall not be adversely affected by prolonged contact with treated or untreated water. It is well known that iron pipe is attacked by soft water,³ particularly at the screwed joints, and when water contains dissolved carbon dioxide voluminous deposits are formed which may lead to blockage of service pipes. The roughness of

the bore of iron pipe also encourages rusting and the adhesion of scale. Lead is considered safe with hard water but is not safe with untreated soft water. Copper is normally satisfactory except in those cases where the water is acid in character, when the pipe is attacked and the water from it is given a greenish tinge. Polythene is not corroded by potable water supplies nor is it affected in any way by sub-soils considered to be corrosive to metal pipes. Lead pipe is heavy and has little mechanical strength. It can deform under its own weight and the pipe is easily distorted. Copper has adequate mechanical strength but owing to the thin gauge of the material, the bore is easily deformed by rough handling. Iron pipe is mechanically strong but is heavy when compared with copper or polythene. Polythene pipe on the other hand is lightweight and being resilient will withstand careless handling without permanent distortion, but some care must be taken with the supporting of polythene pipes particularly if extruded from low density polythene if sagging between supports is to be avoided.

Lead, copper and galvanized iron are all relatively good conductors of heat and pipes made from these materials must be lagged if freezing is to be avoided. Polythene is a good thermal insulator and water contained in unlagged pipes of polythene will take much longer to freeze than when contained in metal pipes. Experiments have shown that polythene pipes made to approved British Standards⁴ do not burst when contained water is frozen and thawed in them for a large number of cycles. Table 27.1 compares the properties of low density polythene pipe with those of the traditional materials used for service work.

The United Kingdom development of polythene piping was pioneered by Imperial Chemical Industries, and the first piping was extruded using an air cooling process, in 1944. The idea of using polythene piping for cold water plumbing originated in 1945 and development work started in the following year. By far the greatest effort has been made in

Table 27.1. PROPERTIES OF LOW DENSITY POLYTHENE PIPE COMPARED WITH TRADITIONAL METAL PIPES

Property	Polythene	Copper	Lead	Iron
Specific gravity	0.92	8.92	11.35	7.86
Heat conductivity at 18°C cals/sec/cm/sq. cm. °C	0.0007	0.918	0.083	0.144
Flexibility	Flexible	Rigid	Flexible	Rigid
Corrosion resistance	Excellent	Fair	Good	Poor
Available lengths	500 ft.	60 ft.	60 ft.	18-24 ft.
Tensile strength, lb/sq. in.	1,900	45,000	2,200	50,000
Crushing resistance	High	High	Low	High
Frost resistance	Resists	Probable failure at joints	Will burst after few cycles	Will split
Effect on water	None	Little except in acid conditions	Serious with soft water	Taints

Britain in the development of polythene pipe for domestic water services, but this project has of necessity moved fairly slowly because of the caution shown by local authorities. Until recently there has been over 900 such authorities each with their own water bylaws. In addition, these authorities have no effective central testing organisation and no positive guidance in the development of new materials. The most successful effort has been in the formulation of a British Standard⁴ which deals specifically with the quality and dimensions of polythene pipe made for cold water services. This specification covers material up to 2 in. internal diameter in eleven different sizes. The polythene pipe manufactured in most European countries at the present time conforms to the size requirements of this British Standard which gives a very clear guide as to the type of material at present acceptable to the water industry. More rapid and more promising developments have taken place both in Britain and in the U.S.A. in agriculture, mainly for carrying water from mains in Britain and from jet wells in the U.S. Special stimulus has been given to this application in Britain because it is particularly easy to lay polythene pipe by mechanical means and thereby to reduce considerably installation costs.

Much work has recently been carried out on the use of high density polythene for pipes. The new polymers have greater strength, stiffness and temperature resistance. It appears, however, that all these advantages cannot be exploited simultaneously. Problems concerning stress cracking, especially at elevated temperature, and U.V. degradation have still to be resolved (see Chapter 11). Undoubtedly the new polymers will be used to manufacture pipes, but many queries have to be answered before it can be assessed to what extent they will supplant low density polythene in pipe manufacture.

DESIGN CONSIDERATIONS—LOW DENSITY POLYTHENE

Both lead and polythene creep, and the design of pipes in these materials is based not only on their initial strength but also on long term performances under stress. Indeed, the design of pipes may be based on a limiting strain rather than on the avoidance of fracture within a prescribed time. The creep of polythene depends to a considerable extent on its molecular weight. The creep of lead, on the other hand is influenced by the crystal structure and by the constituents used for a particular alloy.⁵ When polythene is used for highly stressed applications it is usual to specify materials of low melt flow index.

The creep characteristics of low density polythene and some varieties of lead are shown in Fig. 27.1. In all cases the stress was 500 lb/sq. in. The temperature of the lead specimen was 20°C, and the temperature of the polythene specimen was 30°C. Polythene under stress creeps at a very high initial rate and then the values rapidly decrease to a small steady rate. Lead alloys on the other hand have fairly high continuous creep rates. For periods of a few weeks lead has a markedly better creep characteristic than polythene, but after 3 years polythene is superior to

both pure lead and the low creep alloys. These results illustrate importance of conducting creep tests for long periods where material different creep characteristics are being compared. It is, of course, important to remember that had the polythene tests been done at 20°C the creep figures would have been considerably less than those shown. Now in addition to the difference of creep characteristics the point at which failure occurs is also important in the case of lead. Some of the lead alloys will fracture at elongations of 20–30% whereas polythene has withstood elongations of over 300% for at least 20,000 hours. It is apparent therefore that although lead has a superior short time strength

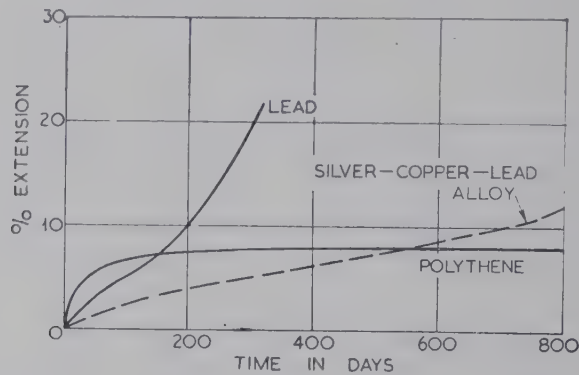


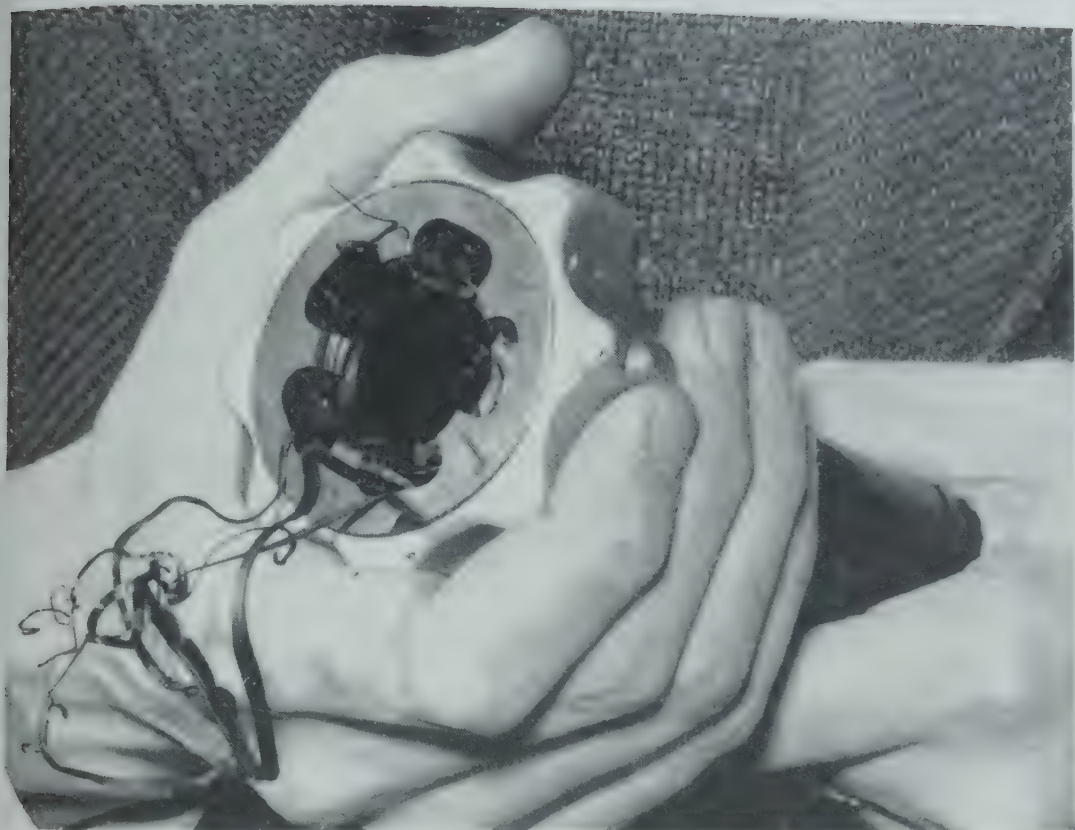
Fig. 27.1. Creep at tensile stress of 500 lb/sq.in. Lead and lead alloy at 20°C, polythene at 30°C

compared with polythene it is a less good structural material than polythene on grounds of ultimate creep and elongation at fracture. The maximum working stress usually laid down for lead is about 270 lb/sq. in. and such figures are reached with large diameter lead pipes used for carrying water. The working stress for low density polythene can therefore be higher, and a figure of 350 lb/sq. in. for low melt flow index materials is considered to be justified. Polythene water distribution pipes which are used extensively in this country, and are described in B.S.1972, operate at mean equivalent working stresses of 300–350 lb/sq. in. the stress being based on a low level of diametric strain during their service life. These stress levels are considerably lower than those quoted from U.S. sources in 1950, but closely agree with the working pressures given in the more recent Canadian government specification.

These design stresses can be translated into a variety of pipe sizes. The most prevalent systems are:—

- (a) the one operating in Britain and the most other European countries which is based on B.S.1972 and
- (b) sizes used on the American continent and based on such specifications as the Canadian Government Specification 41/GP/5 and the United States Department of Commerce, Commercial Standard CS 197/54.

The British Standard sizes are based on the assumption that the pipes will be jointed by some external method of coupling. These methods



Plates 27.1 and 27.2. Lightweight dies for threading polythene pipe



Plate 27.3. Compression sleeve joint; T-joint showing use of flush insert

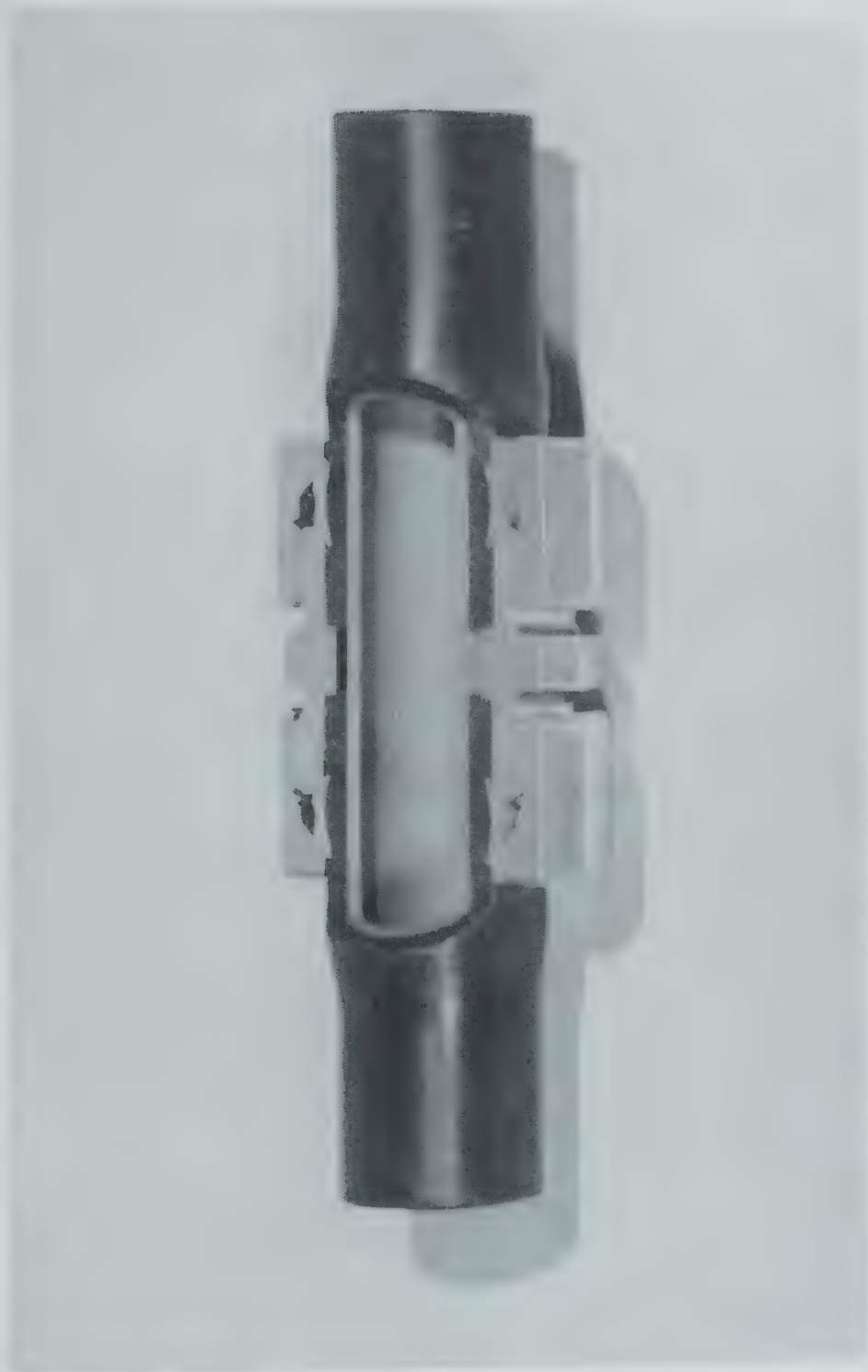


Plate 27.4. Compression sleeve joint; cut-away section of assembly



Plate 27. 5. Polythene tube water sprinkler



Plate 27.6. Normal type mole plough

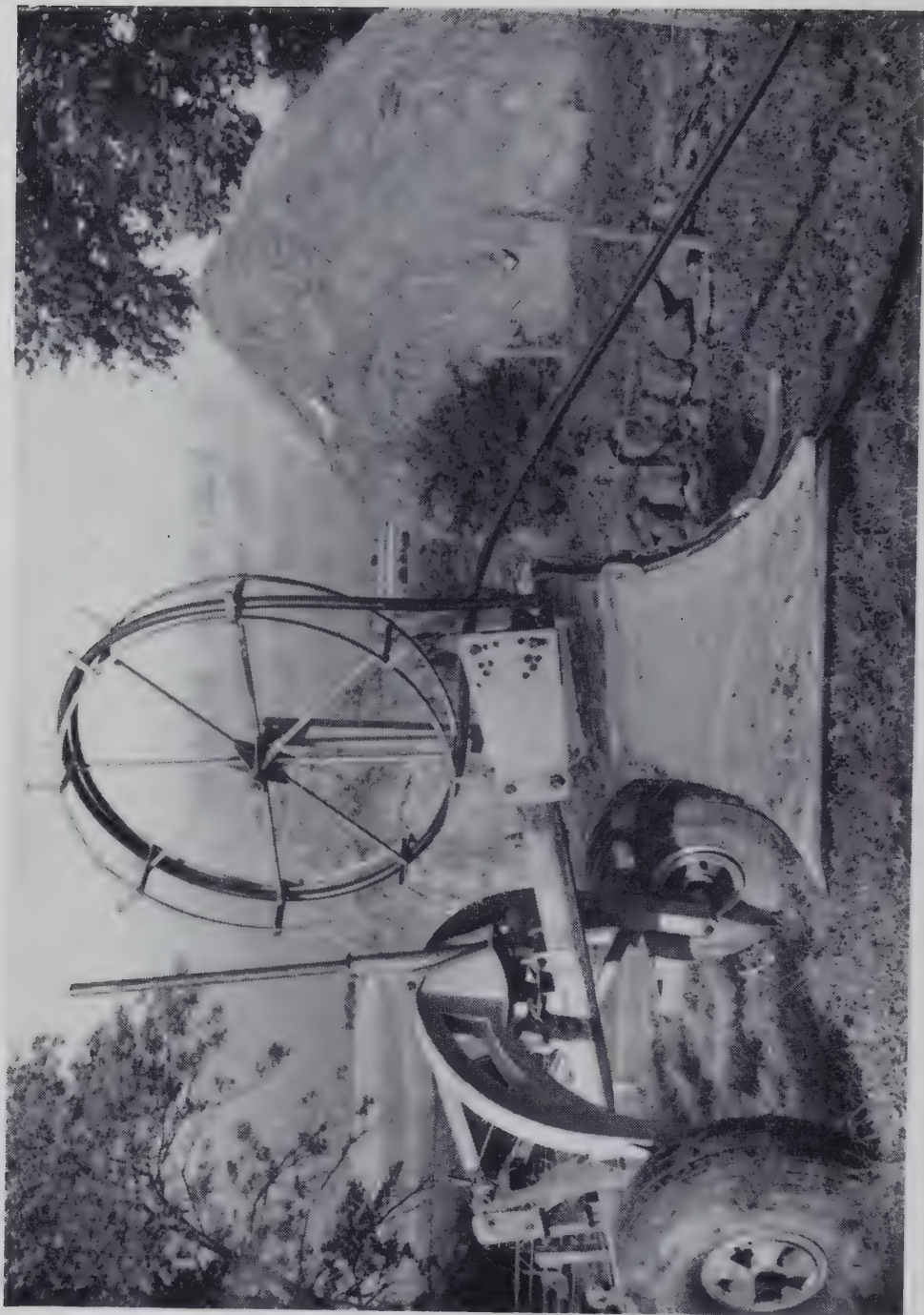


Plate 27.7. Cuthbertson plough for polythene pipe

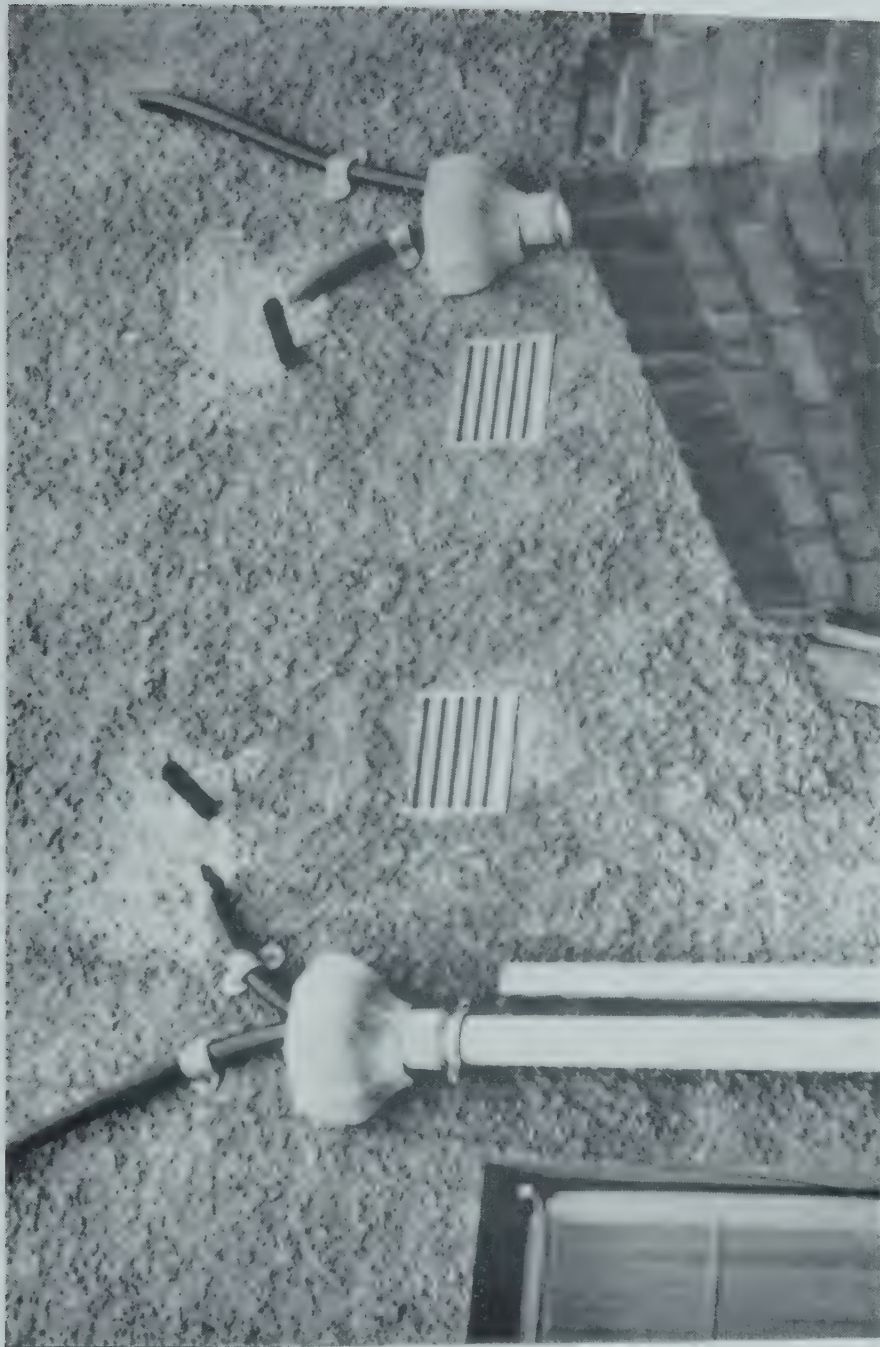


Plate 27.8. Polythene waste and warning pipes installed by Maesteg U.D.C.



Plate 27.9. Fire fighting water supply lines using 6 in. bore polythene pipe

include the use of screwed couplings such as are employed with galvanized iron and compression fittings of the type normally used for jointing copper pipe. Both these methods of jointing are well known to the water industry and accepted by it. The specification names two classes of polythene pipe:—

- (1) Normal gauge suitable for connection by means of compression fittings and
- (2) Heavy gauge pipe having a wall thickness suitable for screw setting to B.S.21 type threads.

The range of sizes covered by B.S.1972 are given in Table 27.2. From these sizes it will be seen that the important dimension is the outside diameter of the pipe.

On the other hand U.S. practice is to use polythene pipe having dimensions similar to those in Table 27.3. Here it will be seen that the inside diameter is more important than the outside diameter. This is due to the fact that polythene pipe is usually joined on the American continent by a serrated insert adaptor and a metal clamp. Thus the inside diameter of the polythene pipe is oversize on this dimension to accommodate this type of insert.

The British Standard includes control of raw materials as well as dimensions. This seems to be an essential requirement if a satisfactory performance is to be given by polythene pipe in service. Emphasis is laid on the importance of having a suitable antioxidant present and on

Table 27.2. SIZES OF PIPE COVERED BY BRITISH STANDARD 1972
HEAVY GAUGE

Nominal bore in.	Nominal outside diameter in.	Tolerances on outside diameter		Wall thickness in.	Tolerances on wall thickness at and point	
		Plus in.	Minus in.		Plus in.	Minus in.
1/4	0.531	0.015	0.005	0.141	0.014	0.003
3/8	0.677	0.015	0.010	0.151	0.015	0.004
1/2	0.840	0.015	0.010	0.173	0.017	0.004
3/4	1.096	0.015	0.015	0.173	0.017	0.004
1	1.346	0.015	0.015	0.173	0.017	0.004

NORMAL GAUGE

1/2	0.686	0	0.022	0.093	0.009	0.002
3/4	1.000	0	0.035	0.125	0.012	0.003
1	1.250	0	0.040	0.125	0.012	0.003
1 1/4	1.500	0	0.050	0.125	0.012	0.003
1 1/2	1.750	0	0.065	0.140	0.014	0.003
2	2.375	0	0.085	0.187	0.018	0.004

POLYTHENE

Table 27.3. STANDARD POLYTHENE PIPE SIZES IN U.S.A.

Nominal size (inches)	Inside diameter (inches)		Wall thickness (inches)
	Diameter	Tolerance	
		Plus Minus	
$\frac{1}{2}$	0.622	0.010 0.010	0.109 ± 0.006
$\frac{3}{4}$	0.824	0.010 0.015	0.133 ± 0.006
1	1.049	0.010 0.020	0.133 ± 0.007
$1\frac{1}{4}$	1.380	0.010 0.020	0.140 ± 0.007
$1\frac{1}{2}$	1.610	0.015 0.020	0.145 ± 0.008
2	2.067	0.015 0.020	0.154 ± 0.008
$2\frac{1}{2}$	2.469	0.015 0.025	0.203 ± 0.009
3	3.068	0.015 0.030	0.216 ± 0.010
4	4.026	0.015 0.035	0.237 ± 0.012
6	6.065	0.020 0.035	0.280 ± 0.015

Table 27.4. RECOMMENDED COILING DIAMETERS IN U.S.A.

Pipe size (inch)	Pipe outside diameter (inch)	Recommended coil diameter
$\frac{1}{2}$	0.840	2 ft.
$\frac{3}{4}$	1.050	2 ft. 6 in.
1	1.315	3 ft.
$1\frac{1}{2}$	1.900	4 ft.
2	2.375	5 ft.

Table 27.5. BRITISH STANDARD RECOMMENDED COIL DIAMETERS

Pipe size (inch)	Pipe outside diameter (inch)	Recommended coil diameter
$\frac{1}{2}$	0.686	5 ft.
$\frac{3}{4}$	1.000	5 ft.
1	1.250	5 ft.
$1\frac{1}{2}$	1.500	7 ft.
2	2.375	10 ft.

the adequate dispersion of carbon black in the polythene as a means of ensuring against degradation of the polythene pipe due to its exposure to ultra-violet light.*

There are considerable differences of opinion concerning the proper coiling diameters for low density polythene pipe. It is standard U.S.

* See Chapter 6.

practice to recommend that the minimum diameter of a coil of pipe is equal to 25 times the pipe's outer diameter. This relationship implies the toleration of a slight degree of flattening of the pipe which is alleged to leave unaffected the pipe's working characteristics. This criterion also presumes the tolerance of 4% strain in the pipe. With this assumption U.S. coil diameters are given in Table 27.4.

At this level of strain some deformation is likely to occur. To avoid this possibility, the British Standard (B.S.1972) recommends coil diameters in which a strain level not exceeding 2.5% is accepted. The resulting specified coiling diameters are given in Table 27.5.

Under these conditions, no permanent deformation of the pipes occur. This is particularly true if the additional recommendation that pipe should be coiled at temperatures not in excess of 30°C is accepted.

DESIGN CONSIDERATIONS—HIGH DENSITY POLYTHENES

High density polythene (0.94–0.96) have higher tensile strength and modulus of elasticity than the classical polymers (density 0.92). In addition they appear to have better creep characteristics and a relatively high softening range. These improved mechanical properties imply that pipes made from the new polythenes will have higher permissible working pressures for a given wall thickness than the established polythene pipes. Short term tests suggest that if we accept the same strain criteria for high density polythene as for low density polythene, then it might be possible to increase the present stress rating of 350 lb/sq. in. to 700–800 lb/sq. in. Further experimental data will be required to confirm this point. It is probable that full use cannot be made of this improvement by reducing the wall thickness of a pipe as the tube might well tend to kink easily when bent sharply.

At the moment the long lengths of polythene tube which can be obtained in one coil (500 feet) is a major advantage in the installation of long water service pipes as it reduces the number of joints and speeds the rate of installation. The pipes made from high density polythenes will be much more rigid and doubts have been expressed about the ability to produce the new material in reasonable sized coils except in the smaller bore sizes.

Thus for agricultural installations and many service pipes underground it is probable that low density polythene pipes will retain their attraction to the water industry. However, for domestic plumbing installations, the greater rigidity of high density polythene pipes will be an advantage, while short straight lengths of pipe will not be a disadvantage in this application. Thus the two types of polythene pipes may prove to be complementary in a similar manner to soft coiled and half-hard straight lengths of copper tube.

Up to the present, the excessive wall thickness required with low density polythene pipes of larger diameters has made them uneconomic except for special purposes. The possibility of having higher permissible

POLYTHENE

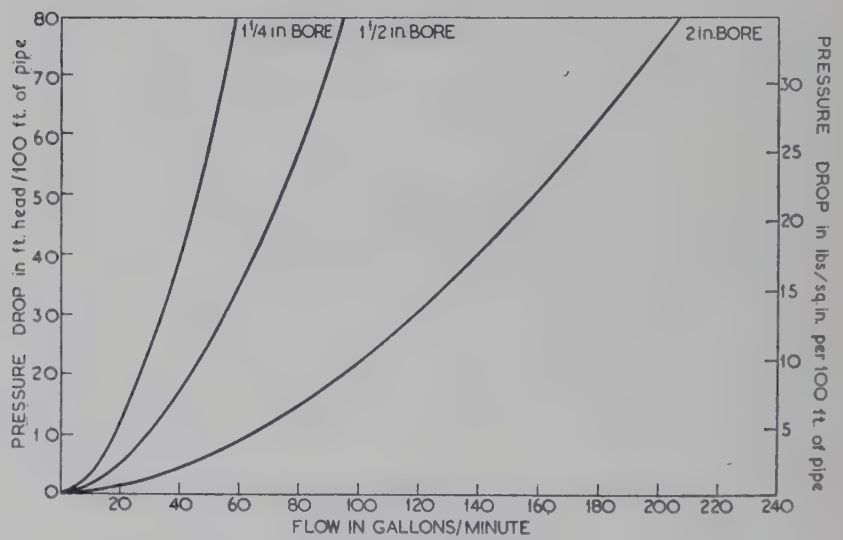
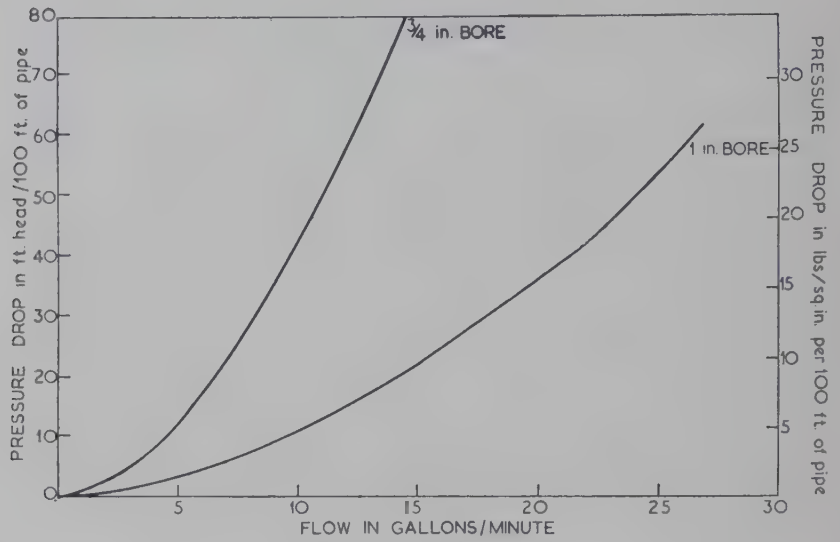
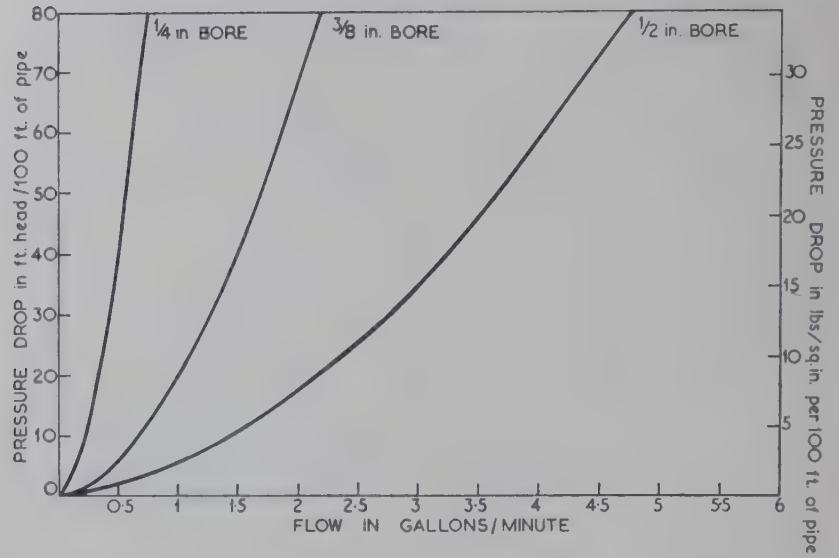


Fig. 27.2, 27.3 and 27.4. Relation between flow, bore and hydraulic gradient

DOMESTIC, AGRICULTURAL AND INDUSTRIAL PIPING

working stresses with high density polythene pipe can materially affect the development of large diameter pipes for such purposes as water mains.

HYDRAULIC FRICTION OF POLYTHENE PIPE

Tests have recently been carried out to determine the loss of head in polythene pipe over a wide range of water flow velocities. As a result of these trials it has been confirmed that polythene pipe is hydraulically smooth. The results confirm that the Blasius formula can be used up to Reynold's numbers of 170,000. When simplified and applied to water at 55°F the Blasius formula becomes

$$V = 103.7 D^{0.7143} i^{0.5714}$$

where

V = velocity in feet/second,

D = internal diameter in feet,

i = hydraulic gradient = pressure/length.

From this formula, it has been possible to derive an expression for the relation between quantity, diameter and hydraulic gradient and from these results, the attached graphs have been plotted (Figs. 27.2, 27.3 and 27.4). The quantity of water passing through a given diameter pipe for a specific hydraulic gradient is given by

$$G = 35.85 d^{2.7143} i^{0.5714}.$$

In this case

G = gallons delivered per minute,

d = internal diameter in inches, and

i = hydraulic gradient.

In the graphs, the pressure drop or hydraulic gradient is conveniently expressed in terms of 100 ft. length of polythene pipe and can therefore be reduced from any length of run by simple proportion. Many materials can be considered hydraulically smooth when they are new. These include polythene, copper and lead. The important point is that as polythene is not in any way affected by water of any type passing through it, its flow characteristics will tend to be constant. In the case of most metallic pipes, there is a gradual deterioration with age. In use, metallic pipes, and particularly those made from galvanized iron, may be corroded and suffer from some incrustation and as a result the resistance to flow will be increased not only because of the added roughness, but also because of the bore restriction. In general polythene pipe can be said to be equal in smoothness to the best metal pipes and since it is not corroded, its high performance will remain unaffected with time. The fact that polythene pipe has lower frictional losses than some metal pipes is not a justification for using a smaller diameter than design consideration dictates. The flow characteristics and corrosion resistance of

polythene pipe does, however, obviate any necessity for making the allowance for loss of performance with age.

JOINTING

European practice in jointing polythene pipe has centred round use of threaded fittings and compression couplings made from various metals. In the case of heavy gauge pipe both these methods of jointing are applicable, while for normal gauge pipe only compression fittings are recommended for high pressure work. These joints are as follows:—

Heavy gauge	<i>Screwed fittings</i>	Sockets, unions, etc., in galvanized iron or copper alloy.
	<i>Compression fittings</i>	Non-manipulative, ring type.
Normal gauge	<i>Compression sleeve fittings</i>	Continuous (for straight couplings, especially with corrosive waters).
	<i>Spigot joint</i>	Flush (for tees, terminal fittings, etc.).
	<i>Electrically welded joints</i>	For waste, flushing and warning pipes. For domestic services

Screwed fittings

This gauge of pipe when made in conformity with B.S.1972 can be threaded using standard stocks and dies; the thread cut on polythene pipe should be a B.S.P. taper thread in accordance with B.S.21. The dies should be of the adjustable and guided variety and with them the full depth of thread can be cut in one operation. With the increased popularity of polythene pipe for water services there have appeared various lightweight dies designed specifically for threading polythene pipes. Typical examples of equipment of this type are shown in Plates 27.1 and 27.2. After such a standard thread has been used any normal threaded fittings can be employed for jointing purposes. The British specifications covering these are B.S. 143 : 1938 and B.S. 1256 : 1945. Although these specifications refer to fittings which are for use with steam, water, gas or oil, polythene pipe should be used only for water and compressed air. The first of these specifications covers iron, brass and gunmetal fittings having female taper threads while the second covers fittings having parallel female threads. There is, however, no functional difference between the two types of fittings and they represent a well known and widely used range of couplings. In addition to the standard fittings, special screwed couplings⁸ have appeared on the British market and are gaining wide popularity. This concept of a fitting designed specifically for use with polythene pipe is one greatly cherished by water engineers.

It should be noted that when normal threaded fittings are used with polythene pipe they should be screwed up to a firm hand tightness, which will give a water tight joint. It is not necessary or desirable to use grips or wrenches on the pipe.⁹

Compression fittings

Non-manipulative compression fittings such as those which conform to B.S. 864 : 1945 Type A can be used with heavy gauge polythene

pipe. The fittings using a compression ring are to be preferred to those having conical sleeves or those with the compression surfaces integral with the fittings. Owing to the greater resilience of polythene these compression rings will have to be compressed more than is usual with copper pipe. When the fitting is correctly tightened, the pipe cannot be twisted within its coupling. Since polythene pipe sizes are a compromise between those for copper and galvanized iron pipes it is necessary to use one size larger compression fitting than the nominal bore of the polythene pipe. Joints of the types described are stronger than the polythene pipe under hydraulic pressure.

Compression sleeve fittings

Manipulative compression joints can be made with normal gauge pipe using the fittings described above. The polythene pipe must first be expanded over a short sleeve of copper pipe before the compression ring is fitted into position. Where the water attacks copper the internal sleeve should be tinned.

There are two forms of the sleeve compression joint normally in use (Plates 27.3 and 27.4).

Flush sleeve. In this fitting the end of each polythene pipe should be prepared separately. Once the ring is compressed the polythene pipe can then be used with any like sized fittings. This is of considerable value in service lines which have to be modified after initial installation. This flush sleeve joint has good tensile strength and is particularly recommended for attaching normal gauge polythene pipe to the torpedo of a mole plough.

Continuous sleeve. In this fitting the copper pipe is of sufficient length to pass right through the compression fitting and be connected to both polythene pipes to be jointed. While this version is very suitable for water supplies which are corrosive to copper or brass it does not allow the insertion of T pieces or terminal fittings.

Spigot joints

The spigot type of joint can be used for all forms of low pressure applications on domestic water services. These installations can be flushing, waste or warning pipes. The method of fabrication is similar to that used for the normal compression sleeve joint except that the polythene pipe is pushed over a standard copper alloy tail piece of the same nominal bore. When the assembly cools, a shrink fit joint will be obtained that is satisfactory for low pressure work. If such joints are used for emergency water supply lines then some form of circular clip around the expanded end of the polythene tube will give additional security.

Apart from the above standard methods of jointing which are associated with metal pipes, there are many other satisfactory fittings designed specifically for use with non-metallic pipes. A typical example of this

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class is the NETA full flow fittings used in Australia and the Swa offered in various parts of the U.S.A.

There also exists in Britain an unique range of fittings moulded polythene which allow a polythene installation especially of an indu nature to be designed using only polythene both for pipe work fittings.¹⁰

When the design of pipe sizes was being discussed it was indicated the main method of jointing polythene pipe in the U.S.A. was by insert type couplings. These are mainly based on styrene copolymers. Their name implies, these insert couplings are forced into the bore of polythene pipes and are then clamped on the outside by a stainless steel clamp.

More recently efforts have been made to replace this stainless steel unit by a compression fitting in which the compression ring is rubber and the compressing parts are moulded from styrene copolymers. Due to the fact that the major portion of the polythene pipe used in the U.S.A. has been employed for private water supply schemes, there has been little progress in adapting this insert coupling method of jointing standard water supply equipment such as mains ferrules and stop valves. Some difficulty has been experienced with these moulded plastics fittings during field trials due to the fracture of the fittings. Brass adaptors of similar pattern solved the problem.¹¹

Electrically welded joints

Finally there has been introduced recently a range of polythene injection moulded fittings. These fittings incorporate a nickel heating element. Through these elements sufficient heat can be generated locally to fuse the inner surface of the polythene fitting to the outer surface of the polythene tube. A 6-volt electrical accumulator is used as the source of supply. This type of fitting, which is much smaller and neater than conventional metal fittings, will increase the acceptability of polythene tube for internal domestic water services.

APPLICATIONS

At the present time low density polythene pipe is being used for the following range of applications:

1. Agricultural water supplies.
2. Domestic water services.
3. Industrial and specialized applications.

Agricultural water supplies

Agricultural water supplies are required for many purposes including live stock, dairying, fruit spraying and the irrigation of market garden crops. The U.K. Ministry of Health Working Party on small diameter pipes¹² estimated that there are 24,000,000 acres in England and Wales under crops and grass and that, on the average, approximately 45 feet

of pipe are used per acre watered. It is assumed that if half this acreage is still in need of better water supplies, approximately 10,000 miles of pipe would still be required. This gives some slight measure of the task involved in providing an adequate agricultural water supply system. The Working Party report quotes an estimate that 1/6 of England consists of formations where a rapid corrosion of metal pipes would occur and another 1/6 where corrosion may be serious. This major problem of soil corrosion over a wide area of the country can be adequately solved by the use of polythene pipes. Polythene pipe is being used to an ever-increasing extent in conjunction with such systems of husbandry as strip grazing. In this process controlled areas of grass-land are provided for cattle, the area being closely defined by the use of electric fences, which are moved at specific intervals of time. To make this system completely successful it is also necessary to have a portable water supply. Polythene pipe is assisting greatly in achieving this ideal of providing water where it is wanted.¹³

More recently work has been undertaken on the use of polythene pipe for irrigation lines. Polythene spray lines are considerably more resistant to the corrosive effect of water than conventional metal pipe lines. Conventional metal pipe lines have usually to be fitted with special spray nozzles whereas polythene pipes need only to be pierced at the appropriate intervals to give spray patterns of the type shown in Plate 27.5.

It has been reported that polythene pipes suitably perforated with larger diameter holes have proved successful as land drainage units.¹⁴ This latter application will tend to become more widespread as the price of polythene is reduced to a level at which these perforated pipes will compete economically with standard earthenware drains. Even now the use of continuous lengths of perforated polythene drain pipe is economically feasible where conventional methods have proved unsuccessful. This is the case where soil drainage results in ground shrinkage and consequent displacement of earthenware drain units.

Pipe laying. Mole ploughing has been found to be a particularly satisfactory method of laying polythene pipes for rural water services. As such pipes can be obtained in coils of up to 500 ft. lengths, underground runs can be made which have only terminal joints. Mechanical joints at 500 ft. intervals can be made in trenches and these can be inspected under pressure before the system is filled in. This aspect is regarded as important by many water engineers who object to this system of mechanical laying on the grounds that buried joints cannot be inspected after they are laid in the ground. In general, any soil that can be mole drained is satisfactory for the mole ploughing of polythene pipe. The flexibility of low density polythene is a great advantage in that curved paths can be followed and only short entry trenches are necessary. Laying speeds of over 200 ft. per minute are by no means uncommon, the controlling factor being the power available for moving the machines,

since the polythene pipe requires only minute extra traction. In addition to the normal mole ploughs (Plate 27.5) which pull the pipe through the ground, other ploughs have been developed and adapted especially with polythene pipes. An example of this is the Cuthbert plough illustrated in Plate 27.7. The polythene pipe can always be connected to the mole plough by one of the methods previously described. The actual joint used will, of course, depend on the gauge of pipe.

Jet wells. In Britain water mains are being laid in rural areas at a fairly high rate. In other parts of the world the jet well is a more important source of supply, and it is estimated that 250,000 wells are sunk in the U.S.A. each year. The jet pump is an economical means of raising water from deep wells and bore holes in conjunction with an ordinary centrifugal pump which normally has a maximum suction lift of 27 ft. The jet pump which is suspended on the pipe work and submerged in the well or bore hole is a simple unit with no electrical connections and no moving parts.¹⁵

By the use of polythene pipe in conjunction with such units it is possible to eliminate the high cost in jet well installations. It is now possible to have an installation using continuous length of pipe for both the down and rising mains. The use of polythene pipe eliminates complex troubles which might result from the corrosive conditions existing in jet wells.

Domestic water services

The use of polythene pipe in water supply systems can be divided into three main categories:—Service and communication pipes; distribution pipes; and waste overflow and flush pipes.

Polythene pipe is being used in Britain for both service and communication pipes to an ever increasing extent. The method of jointing previously described allows conventional water service units such as manholes, ferrules and stop-valves to be employed. In such centres of building activity as the new town of Welwyn Garden City polythene pipes have been used exclusively for communication pipes by the local authorities since 1953. Similar large scale work has taken place in many other parts of Britain.

For water services inside domestic dwellings, the properties of corrosion resistance and lightness of weight are not so advantageous, and polythene pipe has not been used extensively. So far polythene pipe has not been used for hot water systems, partly because of its relatively low softening point, partly because of its high coefficient of expansion, and finally because of the more attractive appearance of copper pipe. The use of irradiated or high density polythene for pipe manufacture might extend the indoor usage as the latter material appears to have increased rigidity and both types of piping would be more resistant to high temperatures. The problems associated with internal domestic plumbing systems made of polythene pipe have by no means been resolved as yet.

Caution is necessary in any consideration of high density polythene hot water service pipes. On no account must the relatively high softening range be confused with the limit of thermal load. In addition, the problems of high expansion values and the need for considerable thermal stability of any polythene tubes remaining in use for a long time at elevated temperatures have still to be resolved.

Polythene pipes have been used extensively for waste pipes and Plate 27.8 shows that polythene systems conform closely to standard practice. These applications are technically sound and economically advantageous due to the excessive cost of lead which was the accepted conventional material for this application.

Industrial and specialized applications

In the U.S.A. there is a fairly large application for polythene pipe in mines, chiefly for conveying acidic waters out of the working face of the mine. Neither high temperatures nor high pressures are involved and the flexibility and availability of long lengths of polythene pipe make it cheaper to instal than steel. It has been estimated that the 1953 consumption for this application was 650 tons. In the United Kingdom there is not potentially the same kind of application. There is, however, a general resistance in the U.K. to any material which can be declared as inflammable, as the explosive hazard is greater in U.K. than in U.S. mines. However, there are many surface applications connected with mining such as estates, administrative buildings and pit-head baths.

Polythene pipe is not used to a considerable extent in chemical plant* due to its temperature and pressure limitations at elevated temperatures. However for laboratory drainage complete polythene systems in which moulded polythene fittings are used are becoming increasingly popular.

There is a large scale and important application for 6 in diameter polythene pipe (Plate 27.9) for emergency water supplies and fire fighting, a project which has been sponsored by the Ministry of Works. The pipe is stored in 18 ft. lengths and has been designed to withstand pumping pressures of 120 lb/sq. in. for periods up to 24 hours continuously. It has the advantages of very light weight, flexibility, resistance to corrosion and speed of assembly in long lengths. One man can carry two 18 ft. lengths of this pipe. This pipe can not only be used for emergency fire fighting duties but can also be employed for flood drainage. It has already been proved successful in this latter application. This special industrial pipe is manufactured to a detailed specification which not only defines the performance of the finished pipe but also the properties of the raw material from which it is made.

Polythene pipe is suitable for a wide range of specialised applications and among those which have been reported as successful are the following:—radiant heat installations in concrete floors; sewage disposal; skating rinks; effluent disposal; beer piping; drainage; golf course irrigation; conveying water treatment solutions; electrical ducting.

* See Chapter 28.

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The greater rigidity and form stability of high density polythene coupled with the traditional good chemical resistance of polythene make the product even more acceptable for chemical plant work. This new material may prove a serious competitor to unplasticized polythene in this field. However, the coefficient of linear expansion of the high density polythene is of the same order as for low density polythene so that the expansion problems characteristic of high temperature applications of plastics still exist.

All these applications, some of which are still in the development stage, add up to an extremely promising future for polythene pipe in its present or in modified form. It is the newest arrival in the field of water supply practice and seems destined to replace at least some of the conventional materials.

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CHAPTER 28

CHEMICAL PLANT

T. A. STANLEY

IN recent years polythene has been used increasingly in the chemical and allied industries because it has very good chemical resistance and is particularly easy to fabricate. The significance of this unusual combination of properties was no doubt appreciated before the war but for many years the entire output of this strategic material had to be used for important electrical applications that could not otherwise have been developed. After the war production of polythene was increased so that it became possible to consider other technical applications. Naturally the availability of a material of exceptional resistance to inorganic attack, and capable of being welded with quite simple equipment, aroused a lively interest in the chemical industry. This interest was also stimulated by shortage of traditional materials at a time of rapid expansion in the industry and when existing plant had to be replaced or given a further extension of life. In addition post-war surveys of the German chemical industry made it clear that thermoplastics, notably p.v.c. in this case, had already been used extensively and successfully.

Unfortunately there was not enough polythene to satisfy the many applications then being developed in various industries and the natural rate of progress of the material in the chemical industry was undoubtedly hindered. It is true, of course, that much technical skill was devoted to making the best use of the small amount of material that was available, and the enforced low initial rate of development may not have been entirely a disadvantage.

To begin with, the only wrought forms of polythene were sheets of about 6 sq. ft. and tubes of up to 12 in. diameter, usually in straight lengths. With these, tanks could be lined and pipe lines constructed. Later on more material became available and the range of wrought forms also increased. For example larger sheets were produced and these reduced welding time in tank lining applications. The range of sizes of tube also increased and smaller bore tubes began to be produced in coils of great length which in turn reduced installation costs. Foil became available and was used as a flooring underlay, and at the same time a whole range of injection moulded articles appeared which superseded many items of laboratory glassware.

Because of the particularly high resistance of polythene to attack by inorganic media, and susceptibility to attack by some organic fluids,

polythene tended to be used in plants mainly handling acids and salts. For example, the electroplating trade found polythene largely useful and the material was also used for drains and new pits dealing with factory effluent having a low organic content. The resistance of polythene to soil conditions aggressive to metal pipes made the material most attractive for underground water services. In addition to this resistance to attack by soil and water the material has many important advantages compared with metal pipes. For instance, its flexibility, lightness and great length of coils simplified installation and reduced fitting costs. With a gradual reduction in the price of polythene and a tendency for metal prices to rise, the position of polythene in water distribution has become firmly established. Although water applications used to be grouped with others involving industrial chemical problems, they are now so extensive as to warrant separate consideration and they are dealt with in Chapter 27.

Although the quantity of polythene used in chemical plant is of great commercial importance, the technical contribution made by this material gives it a special merit. The applications usually involve the use of equipment of an individual nature, as, apart from laboratory glassware, few items are mass produced, and extensive fabrication is the general rule. Because of the diverse nature of installations in industry, a wide range of sizes of each of the wrought products has to be produced and this has led to the development of firms who specialize in such products. The fabrication side of the industry is now well catered for and many distinct types of fabricator exist. First in the field were specialist firms who dealt exclusively with thermoplastics and in some cases technical direction was given by men who had previous Continental experience in the use of plastics in chemical plant. Subsequently, larger firms which dealt with a variety of traditional chemical plant materials, added polythene to the range of resistant materials offered. The third type of fabrication occurred in the chemical industry itself, as many large firms had a sufficient number of applications to justify the training of staff to deal exclusively with polythene and other thermoplastic materials. For example specialist workshops exist in a number of heavy chemical, textile and pharmaceutical firms.

Some of the factors which influence the use of polythene in chemical plant have been dealt with in earlier chapters of this volume; mechanical and chemical properties have for instance been described in considerable detail.*

In this chapter these properties, as they affect chemical plant work, are briefly recalled, and in addition availability, cost and the relationship of polythene to other chemical plant materials will also be discussed. The special fabrication techniques largely peculiar to chemical plant work were not described in Part II of this book and these will also be dealt with in this chapter. Finally a number of typical applications of polythene in chemical and allied plant will be described.

* See Chapters 9 and 10.

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POLYTHENE AS A MATERIAL OF CHEMICAL PLANT CONSTRUCTION

The use of polythene in chemical and other industrial plant is naturally influenced by the wrought forms in which it is available, by cost and by

Table 28.1. FORMS OF POLYTHENE USED FOR INDUSTRIAL APPLICATIONS

Form of polythene	Method of manufacture	Sizes	Remarks
Sheet	Moulded	$\frac{1}{8}$ in. to $\frac{1}{2}$ in. thick. Area up to 8 ft. \times 4 ft.	The most widely used sheet product.
	Cast	Any thickness. Area up to 12 ft. \times 3 ft.	Made by slitting centrifugally cast tube. Inferior mechanical properties to moulded sheet.
	Extruded	About 30 in. width. Any length	Extruded sheet tends to be oriented and may revert on being heated or welded and is rarely used.
Tube	Extruded	Up to 2 in. bore Up to 500 ft. length	To B.S. 1972 and B.S. 1973.
	Extruded	Up to 12 in. bore Up to 10 ft. length	To B.S. 1973.
	Centrifugally cast	Up to 48 in. bore Up to 3 ft. length	12 ft. lengths have been made. See Chapter 20.
Block	Cast or extrusion moulded	Up to 4 in. thick	
Rod	Extruded	Up to 1 in. dia. continuous lengths	
	Extrusion moulded	Up to 3 in. dia. 1 ft. length	
Welding filler rod	Extruded	$\frac{1}{8}$ in. dia. and to order	Available in coils and packs.
Flat film	Extruded	0.0012–0.010 in. thick. 6 ft. wide	
Tubular film	Extruded	0.0012–0.010 in. thick. Layflat width up to 6 ft.	
Adhesive tape	Extruded	$\frac{1}{2}$ in. to 8 in. wide	Has a chemically resistant polyisobutylene adhesive backing. Can be used for protective wrapping and also for identification since it is available in a range of colours.

performance. These aspects are discussed in this section and comments are made about the relation of polythene to other mater construction.

High density polythenes have been excluded from the discussion they are not yet established materials for the construction of che plant.

Available forms

A considerable range of wrought forms is used for industrial a cations and these types and limiting sizes are given in Table 28.1.

In addition to these basic forms of material there is an extensive r of pipe fittings, and a large number of items of laboratory ware produced in polythene.

Costs

A comprehensive price list covering the many product types and s would be beyond the scope of this chapter and only typical figures the major product is given in the following comparison:

Product	Price per lb.	
	s.	d.
Film	5	3
Tube in coils	7	0
Moulded sheet and large extruded tube	11	0
Block and rod	15	0

Prices, as with many other materials, are given on a weight basis a when making cost estimates it is often helpful to remember that 30 in. of polythene weigh 1 lb. It is of course particularly necessary take into account this unusually low density when making price co parisons and Tables 28.2 and 28.3 show how polythene and so metals, which can be functional alternatives, compare on a basis of bo weight and volume.

The cost of completed installations naturally depends on the sca and complexity of the plant. As a rough first estimate however, t cost may be taken to three times that of the material where considerab

Table 28.2. RELATIVE COSTS OF BASIC FORMS OF METAL INGOTS AND POLYTHENE GRANULES

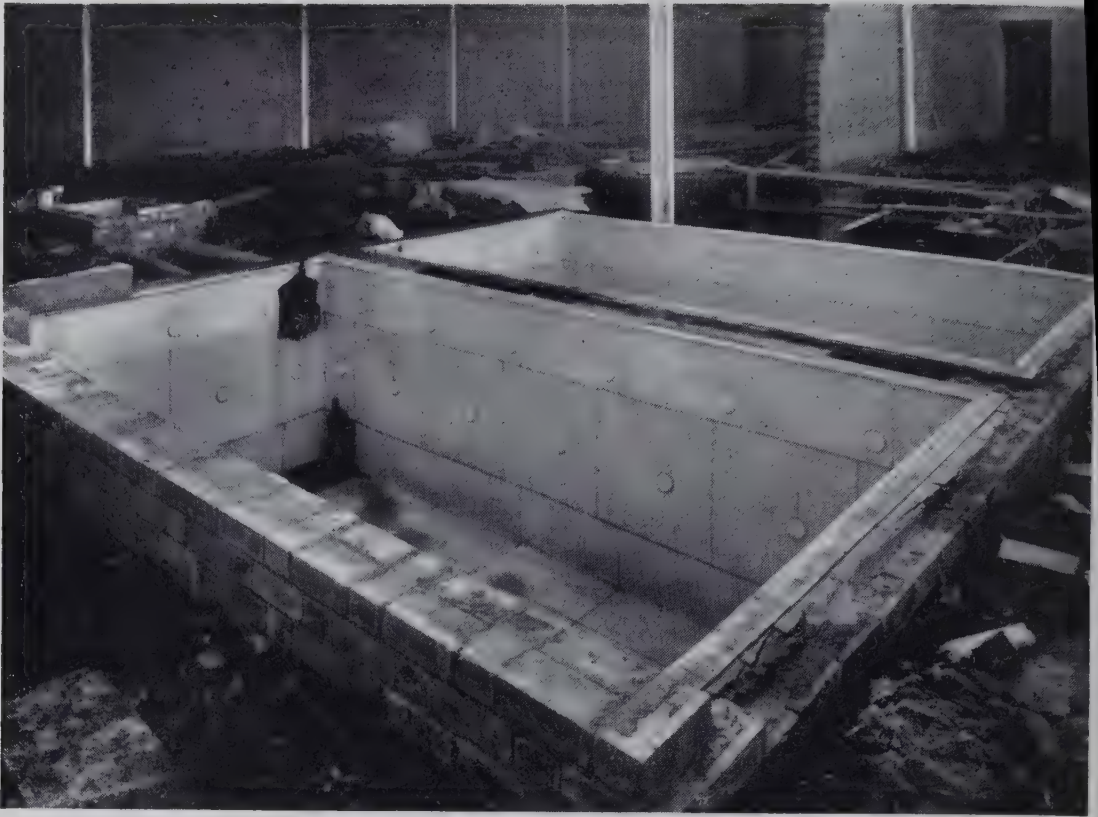
Weight basis		Volume basis	
Lead	0.23	Polythene	1.0
Aluminium	0.40	Aluminium	1.1
Copper	0.68	Lead	2.8
Polythene	1.0	Copper	6.5
Nickel	1.1	Nickel	10
Tin	2.3	Tin	18
Silver	19	Silver	220



Plate 28.1. Welding of tank lining (Courtesy Prodorite, Ltd.)

Plate 28.2. Moulded pipe fittings (Courtesy Folkard-Ferry, Ltd.)





*Plate 28.3. Industrial effluent treatment tanks 15 ft \times 7 ft \times 5 ft.
(Courtesy I.C.I. Metals Division and Prodorite, Ltd.)*

Plate 28.4. Brine pipeline (Courtesy Palethorpes, Ltd. and Tenaplas, Ltd.)





Plate 28.5. Fume ducting (Courtesy Rediweld, Ltd.)



Plate 28.6. Effluent drain with 12 in. bore (Courtesy I.C.I. Billingham Division)

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Table 28.3. RELATIVE COSTS OF WROUGHT FORMS OF POLYTHENE AND METALS (TUBE, SHEET, ETC.)

Weight basis		Volume basis	
Mild steel	0.04	Mild steel	0.31
Lead	0.15	Aluminium	0.73
Aluminium	0.25	<i>Polythene</i>	1.0
Copper	0.34	Lead	1.8
Stainless steel	0.38	Stainless steel	3.1
<i>Polythene</i>	1.0	Copper	3.3

welding and fabrication of large tube, sheet, block and rod are involved. In the case of pipeline installations where long coils can be used, the total installed cost may be near that of the unlaidd pipe; lower in fact than that of unresistant metal tube because of the very considerable difference in the number of joints required by the two materials.

Chemical resistance

The chemical resistance of polythene has been described in Chapter 10, where polythene was seen to have a resistance of a different order, and in some ways complementary, to that of metals. It has exceptional resistance to acids, alkalis and aqueous salt solutions. Although at normal temperatures it is insoluble in all organic liquids some may cause swelling and some, as well as a few inorganic media, may cause environmental cracking if the material is at the same time under complex stress. It follows that polythene is most widely employed in conditions where aggression is largely inorganic, although the material is by no means confined to such applications. Harder grades of material are preferred to those of lower molecular weight or higher melt flow indexes since they have even better resistance to inorganic attack, much higher resistance to environmental cracking as well as slightly better mechanical properties. By no means all wrought forms of polythene could at present be made available in the very hardest grades and, as uniformity of grade is desirable when welding, the U.K. industry has adopted material of melt flow index 2 for general use since almost all forms can be had in this grade. This grade is highly resistant but not entirely immune to environmental cracking and unnecessary welding and installation stresses should be avoided if this unusual type of attack is likely to occur. Black compound is often preferred to natural material for chemical plant. Both are equally easy to weld but the pigmented material has an advantage since it is suitable for external exposure and because the antioxidant it contains can still give protection if internal installations are to be operated at well above room temperatures.

The resistance of polythene to a large number of chemicals has been tabulated in Chapter 10. Much of these data will have been obtained from laboratory tests which naturally cannot always indicate how an actual installation will behave. For example a comparatively slender

laboratory specimen may fail under circumstances which would not affect a robust pipeline. Conversely quite small proportions of aggressive liquid may sometimes alter the character of an apparently harmless mixture. Because the performance of installations can always be predicted from small scale tests users sometimes find it advisable to simulate more closely the scale and conditions of operation in tests.

Mechanical properties

Mechanical properties of low density polythene differ considerably from those of traditional materials and need to be understood if the material is to be fully exploited. These properties have been described in Chapter 9, but the particular aspects which influence chemical plant design are worth recalling. Polythene has exceptional toughness and ductility although the tensile strength of 2,000 lb/sq.in. is no greater than that of lead. Because of this modest strength there are few structural applications. Tanks and vessels are almost invariably given support, the polythene usually being in the form of a liner. Where the material is under continuous load it is necessary to make allowances for the fact that polythene creeps. A primary "load accepting" extension is followed by a very slow rate of secondary creep and designs are usually based on the limiting strain that can be tolerated during the lifetime of the unit. The maximum working stress for indefinite operation at room temperature is usually taken as being about 350 lb/sq.in. Higher stresses can of course, be used for short periods, as the primary extension is largely reversible. The results of laboratory tests suggest that higher working stresses will be possible with high density polythenes.

The strength of polythene decreases as temperature increases, although the rate of deterioration is not rapid as with some thermoplastics. However, because of this decrease in strength, and because of increased activity of aggressive chemicals at higher temperatures, it is not usual to operate above about 60°C. Although this is a widely accepted limitation, some special applications have made use of polythene pipeline for carrying liquids at over 90°C. The polythene naturally had a limited life but, in the particular circumstances, it was superior to that of other materials. The high density polythenes have higher softening points than the established polythenes and this allows moulded components to be steam sterilized without risk of distortion. Neither type of material is immune to embrittlement if subjected to high and continuous temperatures.

Polythene has very high resistance to erosion, abrasion and impact. Normally, of course, this is an incidental advantage which helps to extend the life of industrial plant but there are a few applications in which these properties are of primary importance and a few examples are given at the end of this chapter.

Competitive position

The choice of material for any chemical plant depends on many factors, and, as there are so many types of plant, only the broadest

generalizations can be made when comparing polythene with other materials.

Although the chemical resistance of polythene has been described as being in some respects complementary to that of metals, direct competition between the two materials does arise. An example of this in the corrosion field is of course the large scale use of polythene for underground water supply in which almost all the traditional materials were metal. There are of course also many strictly chemical plant applications in which polythene and lead or stainless steel are functional alternatives. Polythene is naturally excluded for high temperature applications, but it has better resistance to inorganic materials at normal temperatures and is likely to have a lower installed cost than either of these metals. Polythene also competes with a considerable range of other plastics and non-metallic materials. Most of these materials tend to be used to protect a metal structure which is intrinsically cheap if it does not have to be resistant. The most important of these surfacing materials are rubber, polyvinyl chloride, and related copolymers, both plasticized and unplasticized, the resin coatings of various types and vitreous enamel. All of these have the advantage that they can be bonded to steel whereas polythene sheet cannot be cemented to other surfaces. In operation this is not a serious objection however and loose tank linings for example behave quite satisfactorily. Polythene usually has better resistance than rubber although the latter can be used at higher temperatures. Plasticized p.v.c. is not widely used for chemical plant but unplasticized p.v.c. is closely comparable in both function and scale of use to polythene. Unplasticized p.v.c. was of course the most widely used thermoplastic material on the continent but polythene was introduced first in the United Kingdom and became firmly established before unplasticized p.v.c. became generally available. Both materials have about the same resistance to chemical attack although polythene is easier to manipulate and fabricate. The application of resin coatings and vitreous enamel require very specialized skills; they are prone to damage but they have a wider range of operating temperature than polythene. Acrylic linings, like those of polythene, cannot be cemented to metal, and, because this material has a lower chemical resistance than other thermoplastics, it is not extensively used for chemical plant.

The thermoplastic polytetrafluorethylene is, of course, unique as regards resistance and range of operating temperatures but it is a highly specialized and expensive material and offers little direct competition to polythene.

Polythene also competes with chemically resistant stoneware, particularly in effluent disposal systems. The stoneware is itself quite adequate as a resistant structure, but joints are an inherent weakness, and in this respect polythene is very much superior because homogeneous welds can be made.

In the future it is expected that increasing use will be made of furane resin coatings and self supporting and resistant structures of reinforced

polyesters. It may also be that resistant coatings capable of very successful application, such as brushing or trowelling, will appear and supplant many existing techniques of metal protection. In the immediate future, however, polythene is likely to continue to be widely used because of its ease of fabrication and because of the extensive experience that has been gained in the use of the material.

FABRICATION

The construction of chemical plant equipment in polythene involves a number of fabrication techniques which bear little resemblance to traditional processes. As with most thermoplastics, the application of heat causes softening of the material to a state when it can be manipulated with simple tools and, in the case of polythene, a number of other fabrication processes are performed when the material is molten. Although the important fabrication techniques are quite simple, there is no doubt that work should be done by experienced operators if consistently successful results are to be achieved. Because these methods of fabrication influence the way in which polythene is used in chemical plant a description of them is given below. Initial trials show that the following fabrication methods will, with little modification, also apply to the high density polythenes.

Machining and forming

Polythene sheet can be cut using a knife and straight edge, while tube may be sawn or cut with pipe cutters. For machining, high speeds and low rates of speed with very keen tools of rounded profile and adequate rake are preferable. Lubricants and coolants are not used although air blast cooling is sometimes used to avoid overheating.

The single curvature bending of sheet, rod and tube is quite simple and the material is heated in boiling water and held in the required position until cool. Heavy sections are easier to manipulate if heated to about 105°C in brine or glycerine baths. If very sharp bends are required in sheet, such as when tank liner corners are being made, it is preferable to heat only a narrow zone of material with a suitably masked strip element and then fold at the molten "hinge". It is important to remember that material which has been shaped when hot will try to revert when reheated to the manipulation temperature.

Double curvature shaping and deep drawing of polythene are practicable and therefore deep containers are usually fabricated.

Welding

Of the several ways of welding polythene the filler rod method is by far the most important. It applies to all normal grades although it is not at present practicable to weld material of melt flow index 0.2. A filler rod, usually of $\frac{1}{8}$ in. diameter, is used and the edges of the sheets or tubes to be joined are given a V section. The grade of the filler rod should

where possible, be of the same grade as the parts to be joined and should never be of a harder grade. The filler rod and the surfaces to be bonded are heated with nitrogen using one of the several hand torches specially designed for the welding of thermoplastics. The inert gas avoids any tendency of the polythene to oxidize, although some operators claim that, if the polythene contains a service anti-oxidant, air can be used for heating. The rod and torch are usually held as shown in Fig. 28.1, and, as the adjacent surfaces melt, the rod is manipulated so that the viscous edges and the rod are fused together. This process requires a fair degree of skill and is usually done by experienced operators, two of whom are shown in Plate 28.1 welding $\frac{1}{4}$ in. polythene sheet to form a

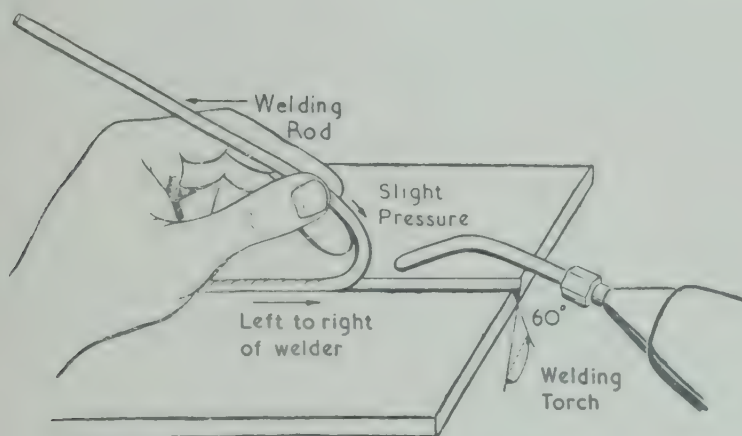


Fig. 28.1. Filler rod welding

tank lining. This welding is satisfactory for joining together sections of $\frac{1}{8}$ in. and above in thickness, and is used for welding sheet and tube and for building up assemblies from moulded components. The strength of welded joints is not much less than that of the parent materials, but the discontinuity at the joint reduces ductility. This reduction is not serious since the extensibility of the parent material is far in excess of that required for the majority of applications. The welding can however induce local stresses which may be undesirable if imposed upon any residual stresses existing in the parts to be joined. Such a combination of stresses could increase the likelihood of environmental cracking if the joint were exposed to circumstances which encourage this type of failure.

The chances of failure will decrease with time, because of stress decay, but if conditions of operation do represent an environmental cracking hazard then it is desirable to anneal the materials in boiling water before and after welding.

Butt welding is the second method of jointing and is usually confined to rod and tube. The ends of the sections to be joined are simultaneously melted by exposure to radiant heat and then pressed together, a slight twisting motion usually being applied to give a more positive fusing of the surfaces. Joints made in this way have about 70% of the tensile

strength of the parent material and butt welded tube joints are stronger than the tube under hydraulic pressure.

Friction welding is the third method and is normally only used to join together injection moulded components of circular shape in certain types of bottle manufacture. The method consists of pressing together two surfaces which are rotating relative to each other so that frictional heat causes them to melt and fuse together.

The welding of polythene film and foil is usually called sealing, and of the many methods used in the packaging industry, only hand sealing is of direct interest in chemical plant. This hand sealing is used for making lap joints in foil used as an underfloor membrane. A domestic iron can be used to heat the double thickness of foil above the melting point so that the layers fuse together. To prevent adhesion of polythene to the sole of the iron a barrier of paper or p.t.f.e. film is used between the foil and the iron. This method can also be used to weld foil to sheet; such joints are leakproof but they have low mechanical strength.

Casting

Flow casting is a technique of limited application and only M.F.I. grade material, of the high polymers, is sufficiently mobile when molten to be used for this type of casting. Small metal containers may be lined with melting material and allowing it to flow round the inside to form a protective skin. Alternatively small self-supporting vessels can be made by having the outer container in the form of a detachable mould. The process is slow and usually only of interest when a few units are required.

Centrifugal casting is used for making tube of greater bore than can be extruded. In this process, the granules are melted in a spinning metal tube which is heated externally. After the granules have been compacted the tube so formed is cooled while still being rotated. Tubes made in this way can be slit to form sheet, and, although such sheet is usually less ductile than moulded sheet, it has been successfully used in some applications. Centrifugal casting was once no more than a laboratory technique for producing small tubes, but the system has now been extended to produce very large bore pipes and the latest methods are described in Chapter 20.

Spraying, dipping and coating

Flame spraying* is a specialized technique for applying a protective layer of polythene to metal surfaces. The polythene, as a fine powder, is forced through a special pistol in which the powder is heated by an oxy-propane flame. The melted particles fuse together as they strike the metal surface which has to be shotblasted to form a suitable key. It is a convenient method for applying a thin layer, particularly where items are of too complex a shape to be covered by a more robust fabrication.

* See also Chapter 23.

covering. Some recent development work has shown that it may also be practicable to coat porous surfaces by flame spraying, satisfactory adhesion being ensured by special undercoats.

Metal articles and containers may also be coated by preheating them and applying powder by dipping,* or from a dispenser, and then fusing the powder to form a continuous layer in an oven. Although the method is simple in concept, it requires careful control and is normally only carried out by specialist firms.

Articles may also be coated by dipping them in molten polythene but again only material of M.F.I. 200, of the high polymers, can be used, as harder grades are too viscous when molten. Although this method was once used on a small scale for coating plating jigs it can be regarded as being superseded by the oven technique described above.

The solution coating of metal and other articles is technically possible but the sparing solubility of polythene permits only the thinnest of layers to be applied, and the method is rarely used.

Tube jointing

There are many sizes of pipe available for chemical plant applications and the most common are listed in British Standard 1973: "Polythene Tube for General Purposes, including Chemical and Food Industry Uses". Because of this extensive range of sizes, several methods of jointing have been developed and the more important are described below.

Where the tubes correspond in size to those commonly used for water services, the jointing methods described in Chapter 27 may be used. These employ standard metal fittings and would be satisfactory in plant where corrosion would not be serious. The continuous sleeve joint, which is sometimes used for water services, although not a break-down joint, has an additional advantage since the sleeve may be made of a resistant metal. Any of these metal fittings may be protected from attack by corrosive atmospheres by wrapping with adhesive polythene tape.

When metal fittings cannot be tolerated other methods of jointing are employed. The end of thin walled tubes of small bore may, for example, be heated in boiling water and expanded over the same size of tube to form a "tafted" joint which can then be filler rod welded. This method of expansion may also be used to join such tubes to metal or glass spigots. Heavier gauge tubes of small bore may also be butt welded together as described in an earlier section. All sizes of tube may be filler rod welded and this method is invariably used for the large sizes of tube when a break-down joint is not required.

Flanged joints are used where it is desired to break a joint, and flanges can be cut from sheet stock and welded direct onto the tube. Then

* See also Chapter 24

again, moulded flanges are available for a number of sizes of tube these have necks so that the weld line occurs some little distance from the rear face of the flange. Moulded fittings are also available. To simplify installation and reduce the amount of fabrication; a collection of them is shown in Plate 28.2.

APPLICATIONS

Because of the wide range of properties, combined with particular ease of fabrication, polythene finds many uses in chemical and other industrial plant. Although the applications are numerous most of them fall into a number of distinct categories and the more important of these, together with a few miscellaneous applications, are described below.

Tank lining

Polythene sheet is used in a number of ways for lining tanks of resistant material. In most cases the tank structure is of steel, although some concrete pits have been lined and even obsolete wooden pickling vessels have been given a new lease of life by adding a liner. Since polythene cannot be cemented to other surfaces, the linings are always of the loose type. It is usual to ignore differential thermal expansion and in almost all cases the lining is made a snug fit in the outer container. An exception to this is where the tank to be lined is of uneven contour then a cement grout may be run in between the tank and lining while the latter is temporarily supported. If a loose lining is to be used with hot liquids it is found that the tendency for the lining to expand and buckle is prevented by the hydrostatic head of the liquid. When the walls of the tank are of a large area it is usual to fix the lining to the tank at a number of points using flat headed bolts in clearance holes over which polythene caps are welded. This type of construction prevents the tendency of the lining to sag when it is empty and an example of the method applied to an effluent treatment tank is shown in Plate 28.3.

The lining process is comparatively simple and consists of welding together sheet edges which are butted together. To reduce welding stresses it is usual to stagger welds in alternate sheet rows and it is convenient to use bent sheet in corners so that welding can be restricted to flat surfaces. The top edge capping can be of flat sheet or of half section tube.

For small linings sheet of $\frac{1}{8}$ in. thickness is used while for large tanks $\frac{1}{4}$ in. may be found more convenient, particularly when pre-fabrication. This pre-fabrication is of course an advantage for a number of reasons as well as the fact that a backing weld can be given to all joints.

These tank linings find many applications, typical of which are effluent treatment tanks, electroplating tanks, pickling vats and metal refining vessels. Operating conditions using low density polythene are limited to temperatures of 60°C. and below, although there are a number

electroplating tanks operating at 70°C. In some electroplating tanks a continuous lining is not used and polythene sheets are suspended around the walls of the steel vessel to reduce both the effects of bi-polar action on the process and the "bath" deposition on the tank walls.

Ducting

Polythene is used for ducting, hoods, exhaust stacks, and other fume extraction applications; installations being built up by welding together combinations of sheet and tubes. The low weight of the material avoids the necessity of very robust support and the resistance to external, as well as internal, corrosion is often an additional advantage in industrial plant. These extraction systems, one example of which is shown in Plate 28.5, can be quite complicated, and the construction of them is naturally confined to skilled fabricators.

Pipelines

Polythene tube is used for handling corrosive fluids and where external corrosion needs to be avoided. The smaller bore tubes are available in lengths of up to 500 ft. and since the material is flexible, pipelines can be installed with great rapidity and at low cost. Polythene tube is used with many fluids and only a few typical examples can be given. It is used for handling acids in road tanker discharge lines, for crop spraying, for conveying brine in the treatment of food (an example of this application is shown in Plate 28.4) and for chlorine injection systems in water treatment and the paper manufacturing industry. With chlorine some attack occurs but the polythene is found to be superior to alternative materials. Sometimes external corrosion is a particular hazard and polythene has been used to replace metal pipes in sewage disposal works of the aerated sludge type because corrosion scale from the metal pipes previously clogged the porous tiles through which the activating air is fed. In some cases polythene is used to avoid contamination rather than defeat corrosion and is, for instance, used to convey demineralized water so that metallic contamination does not occur. Polythene has also been found to be most effective for pneumatic instrument lines since metal scale from the inside of metal pipes can cause failure of the instruments. The substitution has other advantages since the polythene is lower in first cost than the drawn steel tube that had been previously used, jointing costs are very much less and the re-painting maintenance costs for the metal tube are avoided. Polythene tube is also used in the brewing and vinegar trades, particularly for conveying beer from cellar to pump. The natural tube is sufficiently translucent for liquid levels and cleanliness to be observed and it is much cheaper than alternative materials currently in use.

Polythene tube is also used for the pneumatic conveyance of chemicals since it is of high internal finish and because it can be easily installed, with the minimum of joints between entry and exit points. Transparent

tubular film has also been used for experimental pneumatic conveyor systems as flow phenomenon can then be easily studied.

Buried drains

In recent years considerable use has been made of polythene pipe buried drains, especially those handling corrosive effluents from chemical plants. The orthodox materials of construction for these drains include rubber lined cast-iron pipes, and glazed earthenware pipes jointed with special cements; drains of very large capacity are sometimes made of bricks jointed with suitable cements. Drains made in these materials have many disadvantages, usually associated with the joints, and polythene pipes are an attractive alternative to them, except where very large effluents have to be carried.

Polythene pipes can be welded together to form continuous lengths. The resistance to chemical attack from effluents is more than adequate except where certain organic compounds are present; there is no danger of the pipes being attacked from the outside by ground water, soil bacteria or stray electric currents. The welded pipes are flexible enough that there is little danger of fracture due to ground movements or vibration. The need of periodic cleaning is reduced because solids do not adhere strongly to polythene surfaces; and the pipes are robust and light so that handling is easy.

During the last decade many polythene drain systems have been laid and have operated successfully. The diameters have varied between 4 in. and 36 in.* In some cases, depending on the size of the drains and their depth, the pipes have been surrounded in concrete. Where the ground water level is high, it is advisable to anchor the larger diameter pipes into the surrounding concrete to prevent them collapsing inward owing to external hydrostatic pressure. For manholes, fabricated polythene T pieces subsequently surrounded in concrete have been used. In other cases, the pipes have been led into brick manholes, which may be lined with polythene sheet. With pipes up to about 12 in. diameter laying is particularly simple. Long lengths, 150 ft. or more, can be fabricated on the surface and then threaded into prepared trenches, as shown in Plate 28.6.

Cast iron and earthenware drains which have failed in service have been replaced quickly and cheaply by threading long lengths of polythene pipe through them. Excavation is necessary only at a few points along the drain length and this method has been used to replace drains passing below railway lines and in quarries where blasting operations took place regularly.

Resistant membranes

Polythene foil can be lap welded to form a continuous membrane for inclusion in stoneware and concrete structures to prevent possible liquid penetration. Chemical plant floors, plinths, ducts and channels usually

* See Chapter 20.

need to be resistant to the effects of spillage, seepage and storm water. It is not practicable to rely on a jointless monolithic structure and surfaces are frequently of resistant bricks or tiles. These are set in acid resistant cement but due to shock, or general contraction, cracks may occur in the composite structure and corrosive liquids may penetrate. Such penetration can in time cause extensive damage to the concrete sub-floor, foundations and even the steel framework of the building. To prevent this damage an underlay of resistant material can be laid underneath the top surface, and in the past lead or rubber was used for this purpose. It is however very much less costly to use polythene foil and a number of floors have been laid which incorporate this material. Foil of a thickness of about 0.010 in. is used, and, as this is not entirely puncture proof, some precautions are necessary to prevent accidental damage during laying. The foil may be laid on green concrete, preferably containing smooth aggregates, or building paper may be used as a barrier between dry concrete and the foil. Each width of foil is lap welded to the next, as described in a previous section, to form a continuous membrane. The foil is very pliable and it is easy to tailor it around plinths or into ducts and channels. An acid resistant cement is then laid upon the foil and the bricks or tiles set in this cement. This top surface has the necessary resistance to corrosive liquids and has the wearing properties to withstand heavy traffic while the polythene foil ensures that no penetration to less resistant sub strata occurs.*

Polythene foil has also been used as a membrane in sumps and tank. and in reaction towers. In this case it is usually inserted between a resistant brick facing and the steel structure. To simplify working on vertical surfaces it is often convenient to attach the foil to the tank wall for, although there are no cements for polythene, pressure sensitive adhesives can be used. These are based on polyisobutylene and the adhesion is sufficiently good to last during the period of construction.

Laboratory equipment

Polythene is increasingly replacing items of laboratory glassware because the mass production techniques of injection moulding and extrusion blowing has led to an extensive range of low priced laboratory items being available. Polythene containers and vessels are attractive because of indefinite life and the elimination of the hazard to laboratory staffs of glass breakage and the accompanying danger of escaping contents.

Generally the first cost of polythene vessels is greater than that of glass but in many cases, such as that of funnels, the differences are not large and are in any case unimportant when the relative life of the two materials is taken into account.

Thin walled bottles made by extrusion blowing techniques are also being extensively used since flexibility, as in the case of wash bottles, enables the contents to be dispensed by squeezing.

* Cf. Chapter 26.

POLYTHENE

The use of polythene is not confined entirely to small vessels as can be seen from the above. Replacements and even 40 gallon containers have been made. It is probable that these will become more widely used as they ensure lower transport costs and a much reduced handling risk compared with metal containers.

Miscellaneous applications

There are a host of chemical plant and industrial applications for polythene which are not in the categories so far described. In some of these chemical resistance is not of primary concern and a few examples are given below to complete the picture.

Apart from the use of polythene tank linings and insulation plates in the electro-plating industry, there are at least two other interesting applications in this field. Polythene, because of its inertness and low specific gravity, is used in the form of short small bore tubes or pellets for plating bath floaters. The surface of the electrolyte is covered with a blanket of these small pieces of polythene so that fuming and splash are avoided without hindering the entry and removal of anodes and components being plated. This protective blanket not only reduces atmospheric pollution but it also avoids needless loss of expensive electrolyte. Polythene is also used to insulate plating jigs, the material usually being applied by dipping the heated jig in powder and then fusing it in an oven to give a continuous coating.

Polythene is exceptionally tough and some industrial applications take advantage of this property. For example the material is used for hammer heads and also as an alternative to raw hide hammer facing. It is also found to be superior to boxwood for various types of lead beating tools and bossing sticks.

A specialized application of polythene which exemplifies the resistance of the material to erosion is its use for steam condenser tube inserts. A short polythene tube with a belled end is pushed into the inlet end of the condenser tube. This insert is not affected by the entering cooling water, and thus prevents erosion of the metal condenser tube.

CHAPTER 29

HOUSEHOLD GOODS

K. B. BARTLETT

ONE of the most spectacular plastics developments in recent years has been in the use of polythene for household goods produced by injection moulding. Although in the early 1940's there were occasional references to polythene containers, not until 1946 in the U.S.A. and 1948 in Great Britain was there any indication that there might be a large market for polythene moulding materials for use in household articles. From the outset there has been a divergence in British and U.S. views on the place of polythene in domestic mouldings, and developments in the two countries have been on very different lines, with other countries following the lead either of Britain or of the U.S.A. There is now a tendency for U.S. moulders to produce the type of article that is already well-established in Great Britain and for British moulders to introduce articles that have long been popular in the U.S.A., but in considering the history of polythene for household goods it is necessary to treat each of the two major producing countries separately.

DEVELOPMENT IN GREAT BRITAIN

In Great Britain the first polythene household article of any importance to be marketed was the washing-up bowl, which first appeared in 1948. Production in that year was on a very small scale. It is estimated that today there are (excluding variants of basically the same object) over 40 different household articles moulded in polythene in Great Britain and that in six years there has been an eighty-fold increase in the use of polythene for domestic mouldings. Of the annual production of polythene in Great Britain the proportion used for the injection moulding of household goods has risen from a fraction of one per cent in 1948 to well over 20% in 1956.

Part of this consumption is used for such things as colanders, sink tidies, lavatory brushes, soap dishes, soap racks, salad shakers, etc., but by far the greatest weight goes into washing-up bowls and domestic buckets, that is to say into articles of relatively thick section. (It is in this respect that American practice has differed from British, the U.S. moulder having concentrated initially on thin-walled articles.) So great has been the effect of polythene mouldings in the household goods market in Great Britain that manufacturers of enamelled and galvanized iron hollow-ware report that for some of their products demand has ceased completely and that wholesalers and retailers, after clearing stocks of

enamelled washing-up bowls and galvanized buckets in particular restock only with polythene. This has led to the entry into the injection moulding field of more than one old-established British producer of enamelled hollow-ware in an attempt to recover some of the market lost to the moulders of polythene.

The advantages of polythene

That polythene should have achieved this degree of success is now, at the event, cause for little surprise. Consideration of the properties of polythene shows it to have many advantages over the materials formerly used for household articles. In nearly all domestic applications the outstanding virtues of polythene are its low specific gravity, its toughness, its immunity from rusting and chipping, its resistance to moisture and its non-toxicity; to these may be added virtues more aesthetic than technical but no less important for that, namely that polythene articles are noiseless in use, attractive in appearance and hygienic. Other properties of polythene give it advantages in specific applications; for example its flexibility is of value in certain types of containers, its low temperature flexibility in refrigerator accessories, and its chemical resistance in such articles as w.c. brushes and their containers, lemon squeezers and so on. Against these many advantages, however, must be set two disadvantages which, in theory, are serious, but which in practice have created few difficulties at all. These disadvantages are, first, that polythene is a thermoplastic melting at a relatively low temperature and secondly that it is susceptible to environmental cracking when stressed in the presence of some organic polar reagents. Despite this heavy preponderance of real advantages over theoretical disadvantages the first polythene washing-up bowls did not achieve success overnight. Indeed, it was a matter of years before widespread distribution was achieved and before a second manufacturer found it worth-while entering the market.

Distribution channels

In addition to the many trade moulders whose output includes a small proportion of household goods in polythene, there are today some 30 U.K. concerns moulding polythene housewares on a large scale, and they fall into three main categories:

- (a) established moulders who have added polythene household goods to an existing range of products (a range which, in some cases, included household articles moulded in other plastics);
- (b) new moulders who entered the trade primarily to mould polythene domestic ware; and
- (c) established enamelled and galvanized iron-ware manufacturers who have entered the injection moulding field because of loss of business in their traditional lines.

Two principal systems of distribution are adopted. The former iron-ware manufacturers and most of the moulders of category (a) above

that is, those not newly established for the production of polythene hollow-ware, manufacture branded articles which are sold in the main by department stores and by ironmongers, whose supplies are obtained from wholesalers where necessary. These articles are often individually packaged, are offered with point-of-sale advertising matter and consumer literature and are supported by trade and, sometimes, national advertising, principally in women's magazines. Distribution and promotional costs are thus relatively high, and the branded article therefore tends to find its outlets in the higher-priced end of the market. Other moulders cater for the cheaper end of the market, selling their whole output—usually unbranded—direct to the chain stores, reducing their distribution costs by packing only in bulk and not individually, supplying no promotional material and doing no advertising.

Apparently similar polythene articles—for example, two washing-up bowls of identical capacity—are sold at various prices over a wide range with a considerable difference between the prices of the dearest and the cheapest. A large part of this difference can be accounted for by different distribution costs; difference in overheads between one producer and another also plays an important part; most important of all, however, is the wall thickness of the article (and hence the weight of polythene in the moulding), for while the difference in raw material cost is small, the difference in production cycles can be very considerable. So far as the major items—washing-up bowls and buckets—are concerned, a situation of fierce competition now exists. A few manufacturers, in their efforts to reduce their costs, are producing articles of dangerously thin wall, and run the risk of damaging the reputation of the material by producing end-products that may be unsatisfactory in service because they lack form stability under load, particularly at slightly elevated temperatures.

Range of products

The introduction of polythene housewares in Great Britain was achieved almost entirely without large-scale national advertising, either of the end products by the moulders or of the raw material by the manufacturers. The earliest product to gain wide-spread distribution—a branded washing-up bowl—was introduced through high-class department stores, and initially sold at 25s. at a time when a bowl of similar capacity in enamelled iron was priced at about 7s. 6d. Promotion was confined to good packaging, extensive point-of-sale advertising and the exploitation of a trade name already well-known in connection with household articles in other plastics. Early results were adequate rather than spectacular, and it was not until two years after its introduction that heavy demand for this first of the major polythene household articles began. Following this increased demand other manufacturers entered the business, some producing bowls similar to the original, some designing variants of it, and others extending the field of polythene housewares to include entirely new articles. Of 35 British moulders who are known to be producing

polythene domestic ware on a large scale today, 14 are producing washing-up bowls of one type or another. In addition to washing-up bowls, a list of domestic articles moulded from polythene includes:

Babies baths	Cutlery trays	Lemon squeezers	Sink mats
Babies pots	Dog bowls	Measuring jugs	Sink tidies
Bath brushes	Doylies	Milk bottle closures	Soap dishes etc.
Bath trays	Dustpans	Milk pourers	Strainers
Beakers	Egg racks	Mixing bowls	Table mats
Bread bins	Floating nail brushes	Plate racks	Tableware
Brush backs	Flour bins	Refrigerator trays	Toilet brushes
Buckets	Flower pot holders	and dishes	Tooth brush holders
Cake bins	Food covers	Salad shakers	Tumblers
Colanders	Kitchen refuse bins	Sandwich boxes	Waste bins
Cups	Lavatory brushes	Saucers	Wastepaper baskets
Cutlery drainers	and holders.		

This list does not pretend to be comprehensive since the number of domestic mouldings made from polythene grows almost from week to week. With so wide a range of products for so many different purposes it is difficult to draw any firm conclusion on consumer preferences of colour, appearance and finish. The experience of the longer-established moulders of washing-up bowls suggests however that pastel-tinted, natural and pastel-mottled articles sell most quickly. On one point there is unanimity among moulders—the article must be recognizable at a glance as polythene, and heavily pigmented opaque colours that mask the translucency of the material are best avoided. The nearest there has been to sales resistance against any polythene domestic ware so far was against one particular brand which, admirably designed in all other respects, was offered in opaque colours with a matt surface finish, and had the appearance more of surface-painted papier mache than of polythene. Whether the preference for translucent articles will remain when polythene domestic ware ceases to have any novelty appeal must be doubted.

CHOICE OF MATERIAL

Melt index

For very nearly all the polythene household goods made in Great Britain today material of melt index 20 is used. It was thought at one time that types of higher melt viscosity, for example of melt index 7 or 10 would be most suitable for the application because the susceptibility of polythene to environmental cracking when stressed in contact with polymeric media decreases as the melt viscosity increases. Since most of the modern detergents, with which, of course, household goods are frequently in contact, can cause environmental cracking of polythene, theoretical considerations suggest that material of the highest possible melt viscosity should be used, and, in fact, many of the early household goods were moulded in polythene of melt index 2 or 7 to minimize the risk of environmental cracking. The swing toward a melt index of 20 was dictated primarily by commercial considerations. When the market began to be competitive, moulders sought means of reducing time cycle



Plate 29.1. A selection of U.K. polythene articles for the home



Plate 29.2. Polythene housewares moulded in the U.S.A. and Canada



Plate 29.3. Bucket, toilet brush and holder and an oval bowl all moulded in a mottled pastel polythene (Courtesy Halex)



Plate 29.4. Salad washer moulded in polythene by Craxfords Ltd.

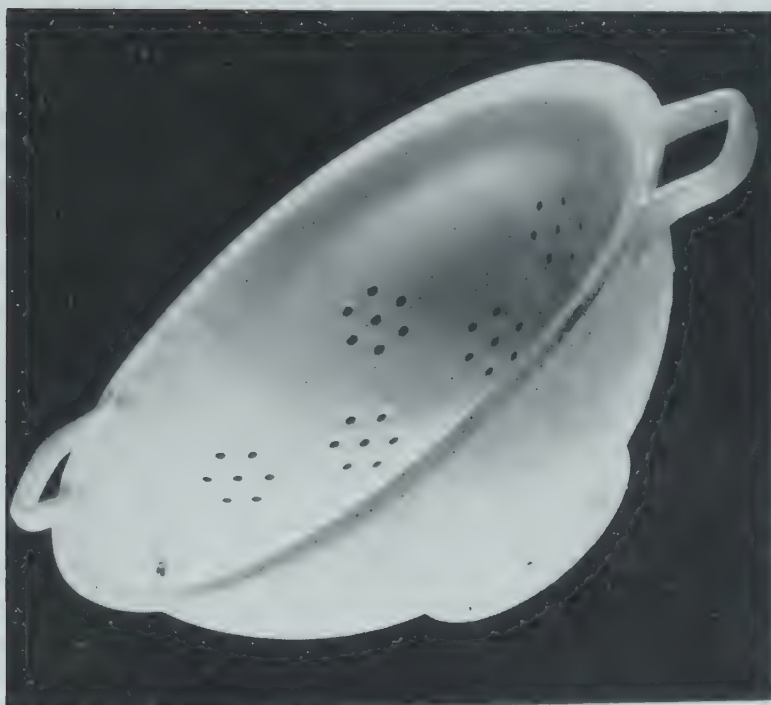


Plate 29.5. Polythene colander moulded by Mendle Bros. Ltd.



Plate 29.6. Dust-pan moulded in polythene by Mendle Bros. Ltd.



Plate 29.7. An example of the popular polythene washing-up bowl

and the most suitable way to do so and at the same time to retain excellent surface finish on the moulding (an important consideration) was to use a grade of lower melt viscosity. Although in laboratory tests samples moulded from polythene of melt index 20 were found to be subject to environmental cracking when stressed while immersed in detergent solutions, practical tests on housewares moulded from this type showed that there was no tendency to cracking. One such test involved the immersion of a moulded bowl in a saturated solution of a well-known brand of detergent for six months, at the end of which time the bowl was unharmed. The explanation of this apparent anomaly lies in the fact that the phenomenon of environmental cracking occurs only on heavily stressed samples. Using polythene of melt index 20 it has proved possible to produce mouldings with a low degree of strain, so that, in normal use, the domestic articles are subjected neither to internal nor to applied stress and hence do not react to the agents which, in different circumstances, particularly those of the standard laboratory test, could produce environmental cracking. Indeed, it is conceivable that articles moulded at high output rates from polythene of higher melt viscosity might be more susceptible to environmental cracking than mouldings from the lower melt viscosity material because of the greater locked-in moulding stresses.

That polythene of melt index 20 has proved perfectly suitable for the moulding of household wares is shown by the infinitesimal number of legitimate complaints of failure made by consumers. Indeed, complaints of failure of any kind—even those subsequently found to be due to abuse of the article by the purchaser—are extremely rare. One moulder, whose experience is probably typical, has estimated the number of complaints from all causes received over several years' production of a variety of polythene household mouldings to be less than one in ten thousand. Credit for this very satisfactory state of affairs is due to the sound policy of informative labelling adopted by the moulder of the original polythene washing-up bowl and by most other moulders since. The labelling generally adopted seems to have achieved its prime purpose of teaching the merits and limitations of the material. Surveys suggest, however, that it has had no great effect in familiarizing users with the name polythene.

Use of anti-static agent

Because polythene is an excellent electrical insulator with high volume resistivity it shows a marked tendency to develop an electrostatic charge which attracts and holds airborne dust particles. The presence of static-held dust on domestic mouldings displayed for sale could act as a sales deterrent and some moulders therefore treat their polymer or moulding compound with a proprietary additive before moulding, to prevent the development of static charge. The additive becomes effective by migrating to the surface of the moulded article and forming an invisible film of high enough conductivity to prevent the formation of

a static charge. This film does not affect the characteristic appearance of the polythene moulding nor does it impart taste or smell. That a majority of moulders do not apply an anti-static treatment suggests, however, that the problem of static-held dust has not, so far, proved great in practice.

CURRENT AND POTENTIAL CONSUMPTION

While no figures are available, it is known that consumption of polythene for household mouldings for the export market has been quite considerable. The light weight and toughness of polythene goods make them attractive export cargoes, since freight rates and breakage are low and several British manufacturers have done and are doing good business overseas. In many territories, of course, the market is a temporary one since overseas moulders themselves are not slow to tool up to produce similar articles; in some smaller territories, however, injection moulding machines large enough for the production of some of the major articles are not available, and these markets are likely to remain open to British exporters—but will become more competitive as moulders in other countries also try to export their products. Consumption of material for mouldings exported and for mouldings sold to hospitals, canteens, hotels and institutions (a smaller but not inconsiderable amount) must therefore, be taken into account in trying to arrive at a figure for the average weight of polythene mouldings per household in the U.K. The estimated quantity of polythene used to date in the U.K. for domestic mouldings (to the end of 1956) is 11,000 tons. Taking 14.5 millions as the number of households in the U.K., the total weight of polythene so far consumed per household is 1.7 lb. so that the final figure, making an allowance of 10% for exported goods as mentioned above, would probably be of the order of 1.5 lb.

A market survey carried out in the London area in April 1955 helps to give a more detailed picture. Just over half (53%) of the housewives interviewed during this survey possessed polythene articles, having an average of 1.6 articles each. The upper income groups had 12 polythene articles for every 7 possessed by the lower income groups, while on an age basis, possession by housewives below 50 years old was twice that of the housewives over that age.

The most common possession was shown to be some form of cups, 20% of all the people interviewed claiming to own them: 17% had bowls; no other article was possessed by more than 8% of the total number of housewives interviewed.

Assuming that a survey carried out in the London area alone can be taken as representative of the U.K. as a whole, the figure for bowls is surprisingly low. If, in 1955, only 17% of the households in the U.K. were equipped with a polythene washing-up bowl, then the total number in domestic use was a little less than $2\frac{1}{2}$ million. Calculations based on production potential would suggest a much higher figure. The maximum known rate of production of a serviceable washing-up bowl in

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polythene of melt index 20 with a single impression mould is 65 per hour, and there are several moulders achieving outputs of 60 to 55 bowls per hour. Thus, a single machine, working continuously can produce up to 1,560 bowls per day, or, making a generous allowance of time off for machine maintenance, 468,000 bowls per year. At least one manufacturer has already claimed to have made over one million polythene washing-up bowls, and there are 14 different moulders, some of them with several machines, producing washing-up bowls of one pattern or another. Thus it would seem that, while the market for polythene bowls is by no means saturated, the rate of production is at present exceeding the rate of sale. This in turn explains why price competition has become so fierce. It seems possible that some producers may be forced to stop moulding bowls in favour of other articles. A trend that is already apparent is towards thinner-walled articles such as bins and food containers.

Future consumption

Estimates of potential future consumption can vary greatly, depending upon the assumptions made, and could be thrown out immediately by the introduction of a single, quick-selling large article. On the basis of the articles already available, a case could be made for putting the potential at any figure between 5 lb. and 12 lb., but what is quite safe to say is that the potential use, per family, of polythene housewares is very much more than the figure of 1.5 lb. which is the average at present.

DEVELOPMENT OVERSEAS

In producing thin-walled articles, British moulders are following U.S. practice just as, in 1954, a U.S. moulder followed British practice and produced a thick-walled washing-up bowl. The first widespread publicity given to polythene for household wares in the U.S.A. was in 1946 when an article appeared describing and illustrating tumblers, mixing and serving bowls (including types with snap-fit lids), and mentioning also soap and toothbrush boxes, refrigerator dishes, and coasters (drip mats). As might be expected, the advantages claimed were the same as those claimed today—toughness, light weight, aesthetic appeal, hygiene and non-toxicity. In addition, mention was made of the absence of plasticizer, of the flexibility which enables a lip to be formed for pouring liquids and enables clinging food to be cleared from the surface, of the lack of brittleness at low temperatures making the containers suitable for deep-freezer storage, and of the advantages of polythene beakers—their resistance to alcohol and fruit juices, their tendency to insulate when containing hot drinks and to minimize sweating with cold drinks. Thus from the start U.S. moulders thought of polythene in terms of containers for comestibles—a class of application for which British moulders showed much less enthusiasm until fairly recently. In choice of material, however, practice in the two countries has followed similar lines, polythene of melt index 20 having been introduced for

moulding in the United States in 1955 and having been received with enthusiasm.

Estimates of future U.S. consumption of polythene for housewares are difficult to arrive at from published figures. In 1954 consumption of all injection mouldings was 32 million pounds, of which some 60%—about 19 million pounds—probably went into housewares. By 1960 total consumption for moulding had risen to about 63 million pounds, and of this the proportion taken for housewares probably rose above 60%. Total consumption of polythene for all injection moulding in 1960 has been estimated at 150 million pounds. If the proportion used for housewares rose to 75%—as well it might—then the annual quantity consumed in the U.S. would be 112 million pounds, a six-fold increase on 1954. Other estimates that have appeared from time to time include “a ceiling in the 50–60 million pounds range” and “20% of total polythene production”—say 190 million pounds. A figure of between 100 and 150 million pounds may well be somewhere near the truth, and the rising trend is already clearly in evidence, from which it would appear that, even in the U.K., there are probably millions of households in the U.S.A. in which polythene housewares are unknown.

In Canada the range of products available seems particularly wide and includes most of those currently available in Britain and in the U.S.A. with certain variants of basic designs besides. A market survey carried out in 1954 revealed that over 70% of the Canadian housewives interviewed used one household article or more of a flexible plastic material (and, therefore, probably polythene). As in the U.S.A., however, early Canadian polythene household goods were of the thin-walled type—tumblers, refrigerator containers, lidded jars and such like—larger, thicker-walled articles coming later.

Elsewhere in the world, for various reasons, the moulding of polythene domestic ware is not yet carried out on the same scale as in Britain and North America, although in some countries this position is likely to change in the fairly near future. There is some production in most of the countries of Northern Europe, generally following the British pattern, and of these producers there are several exporters—Germany on a general scale, Sweden to the other Scandinavian countries and Belgium to the other Benelux countries. Of the Mediterranean countries, Italy produces polythene domestic ware on an appreciable scale, and, while following the British pattern in general, has introduced a number of novel items of interesting design. Production in Spain began early in 1955. In South Africa smaller articles such as beakers are produced on a limited scale, machinery for the production of larger mouldings not being available. There are indications, however, that attempts may be made to obtain injection machines of the necessary size to enable the production of larger articles, following the British pattern. There is virtually no production of polythene domestic mouldings in Asia at present. In Australia and New Zealand production following the British pattern is on a fairly large scale, while in South America moulders tend

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more to follow the lead of the U.S.A. It would seem fair to assume that in nearly all the countries at present producing polythene domestic mouldings there is potential for increase at least on the same scale as in Britain or the U.S.A.

NEW TYPES OF POLYTHENE

All polythene used in the large-scale commercial production of housewares to the end of 1956 was of the low density type. Polythene of this type has a density of about 0.92, has a branched chain structure and consists of both crystalline and amorphous regions. During 1955, evaluation quantities of polythenes of higher density (about 0.94) became available.

Published figures show that the high density polythenes are of greater tensile strength, greater rigidity and higher temperature resistance than the standard materials, and examination of samples shows that they give mouldings of superior surface finish. Moulding temperatures are higher than are required with standard polythenes but are within the range obtainable on standard equipment.

High density polythenes will be a valuable addition to the materials available for the manufacture of polythene housewares. Because their mechanical strength and rigidity are greater than those of standard polythenes it will be possible to mould articles of thinner wall section without reducing their serviceability, and it may also be possible to increase the range of articles made in polythene to include those in which rigidity greater than can be achieved with standard polythenes is desirable. The use of high density polythenes will also make possible the manufacture of articles that must be maintained for long periods at temperatures higher than that permitted by the softening temperature of low density polythene, for example, articles that it is necessary or desirable to sterilize by boiling. It must be stressed, however, that although high density polythenes soften at higher temperatures than low density polythene, they are still thermoplastics and will not be suitable for housewares that must be placed in contact with a flame or on very hot surfaces.

CONCLUSION

Taking then, either British or North American trends, the future for polythene in the moulding of housewares seems very bright. That there will be competition from other plastics in a market that has proved unexpectedly large is undoubted. Among the potential competitive materials are high impact polystyrene, unplasticized p.v.c. and vinyl copolymers and, possibly, certain nylon compositions. It seems likely, however, that while competitive materials may encroach on the market for a few articles, polythene will remain by far the most widely used material, because none of the other materials has the combination of desirable properties possessed by polythene, and because of the outstanding consideration—price. Today polythene in world markets is

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cheaper than any of the other materials likely to be offered for similar domestic mouldings, and there is every reason to believe that it will remain the lowest priced of them all. With a material in which the most desirable properties and lowest price are combined, and with a market, so far, largely unexploited, there seems little reason to doubt that the moulders of polythene household goods will continue to produce to capacity for many years to come.

CHAPTER 30

TEXTILE YARNS AND FABRICS

J. WILLOCK

THE yarns used in the textile industry fall into three groups, namely spun fibre yarns, multifilament continuous yarns and monofilaments. Table 30.1 shows how the various textile fibres fit into the different groups. Of these three groups, spun fibre yarn is the main one from the point of view of quantity produced. These yarns are made by twisting together relatively short fibres into a continuous strand of material. The second group of multifilament yarns covers those threads which are composed of a number of unbroken filaments running continuously from end to end of the thread. In such yarns some degree of twist is inserted in order to bind the filaments together so that the yarn may be handled and processed without disturbing or damaging the individual component filaments. The third group are the monofilaments and these, as the name implies, are used simply as a single filament in the making of textile fabrics.

Low density polythene has been used as the material for the making of any or all of these three types of textile yarns. It can be converted into the short staple fibre for the spun yarns, or into the multifilament or

Table 30.1.—TYPES OF FIBRE/YARN USED IN THE TEXTILE INDUSTRY

Type	Approx. denier* range of fibres or yarns	Approx. diameter range of fibres or yarns (inches)	Example of commercial types
Spun fibre	1-20 (of ultimate fibre)	0.0004 to 0.002	Most natural fibres (cotton, wool, asbestos, etc.) Most man-made fibres (vis- cose acetate, nylon, glass, etc.)
Multifilament	20-2,000	0.002 to 0.020	Only silk of the natural fibres, most man-made fibres as above
Monofilament	8-20,000	0.001 to 0.050	Only horse hair of the natural fibres; man-made —nylon, p.v.c., polyvinyl- idene chloride, polythene etc.

* Denier equals weight in grams of 9,000 metres.

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monofilament yarn form. So far the bulk of commercial production has been mainly confined to the monofilament type, as this is the one to exploit technically, and its production requires the simplest and cheapest plant. Nevertheless staple fibre and multifilament yarns have been made on a small scale and they have very useful technical properties.

MANUFACTURE OF FILAMENT

Polythene as a textile must obviously be classed as a man-made fibre (as opposed to a naturally occurring one). There are three basic techniques of producing a man-made fibre, and each technique follows through three stages. The three stages are, first, converting the raw material into liquid form, secondly extrusion of the liquid through a jet to form the fibres, and thirdly solidification of the extruded fibres. The three techniques of making man-made fibre are called wet spinning, dry spinning and melt spinning according to the way in which the third stage process is carried out (see Table 30.2).

Table 30.2.—PRODUCTION TECHNIQUES FOR MAN-MADE FIBRES

Stage	Technique of production		
	Wet spinning	Dry spinning	Melt spinning
Liquefaction of raw material	Solution by chemical reaction	Dissolving in a volatile solvent	Melting by heat
Forming the fibre	Extrusion through fine holes in a jet		
Solidification of fibre	Coagulation by chemical decomposition	Evaporation of solvent	Cooling
Examples of commercial fibres	Viscose	Acetate	Nylon, glass, polythene

As will be seen from Table 30.2 polythene yarn is melt spun, and it therefore passes through the three stages of melting to form a liquid, extrusion and solidification by cooling. The result is a fibre or monofilament which is too plastic and easily extended to be suitable for use as a textile yarn, and therefore like many other synthetic fibres it has to be drawn to orient the structure and thereby give it suitable mechanical properties.

The actual manufacturing processes developed to date for a commercial polythene monofilament are a novel combination of plastics extrusion and rayon yarn drawing techniques. The whole fibre forming operation involving some half dozen stages from the feeding of the polythene granules into the hopper of the extrusion head, to the collection of the oriented yarn on to bobbins is accomplished in one continuous process.

At the outset it is necessary to select the most suitable grade and form of polythene. Melt flow index 7 is satisfactory although others can also be used.

be used, including high density types as described below under "Current and Future Developments".

As polythene is unaffected by water, normal textile dyeing techniques cannot be used with it. Therefore if the final material is required to be coloured, then the yarns must be spun coloured by the incorporation of suitable dyes or pigments in the extrusion mass. Textile requirements in regard to colour levelness are exceptionally high, as the laying side by side of coloured yarns in a fabric structure is a most searching test in this respect. Coloured polythene moulding powders are a suitable starting material with possible batch variation being minimized by blending in order to maintain maximum uniformity of shade over the required period of production.

The selected raw material is then fed in suitable form to a metal plate with a number of fine holes drilled in it. This is called the jet after the custom of rayon production. The number and size of the holes in the jet are related to the number of yarns which is going to be collected, and to their size or diameter. It is possible to produce monofil in sizes from 0.005 in. to 0.050 in. diameter. This range of diameter incidentally caters for nearly all textile uses, although occasionally finer monofilaments down to 0.003 in. are required for some special purpose.

The hot plastic monofilaments which issue from the jet face have to be cooled and hardened sufficiently to permit them to be handled and drawn satisfactorily in the next stages. Thus, more or less immediately after forming the monofilaments, they are quenched and then pass forward to the drawing and collecting frame. Here the desired degree of drawing, often coupled with controlled relaxation, is carried out in one or more stages by the use of banks of rollers, around which the monofilaments are wound, travelling at different speeds. Here then lies the rayon drawing technique. Mention was made above of the desired degree of drawing and this must be related to the properties required in the final monofilament bearing in mind its ultimate use. The greater the degree of drawing, the higher the strength, the lower the extensibility, the higher the stiffness and the higher the shrinkage on subsequent heating. It is most likely that all these factors will be important in planning the eventual fabric. Thus it will be seen that the production of a textile monofilament yarn from polythene is not simply a matter of extrusion but a complex system of extrusion, drawing and balanced relaxation if need be in order to get the desired combination of properties in relation to the required fabric, finish and end-use.

The final stage of the production process is to collect the monofilaments on to a bobbin or other textile package suitable for subsequent processing in the various stages of fabric manufacture. The monofilament is wound sideways on to such packages to maintain it free from twist.

So far reference has been made only to monofilament yarns in the description of the production cycle. Multifilament yarns are individually composed each of a number of still finer filaments twisted and bound together into a single yarn. At the final stage of production this insertion

of twist is carried out coincident with the collection of the multifilament yarn on to the bobbin by one of the accepted textile yarn spinning mechanisms, usually a cap or ring spindle.

If staple fibre is called for the required number of filaments is combined together to form a tow, which is similar in form to a heavy multifilament yarn, but without twist. This tow is fed to a type of cutting mechanism which accurately chops it into staples or locks of fibre of the desired length. These staples may be opened a little prior to being bagged for delivery to the producer of the spun fibre yarn. A form of floss for fibrous filters can be produced by subjecting the filaments to a controlled twist.

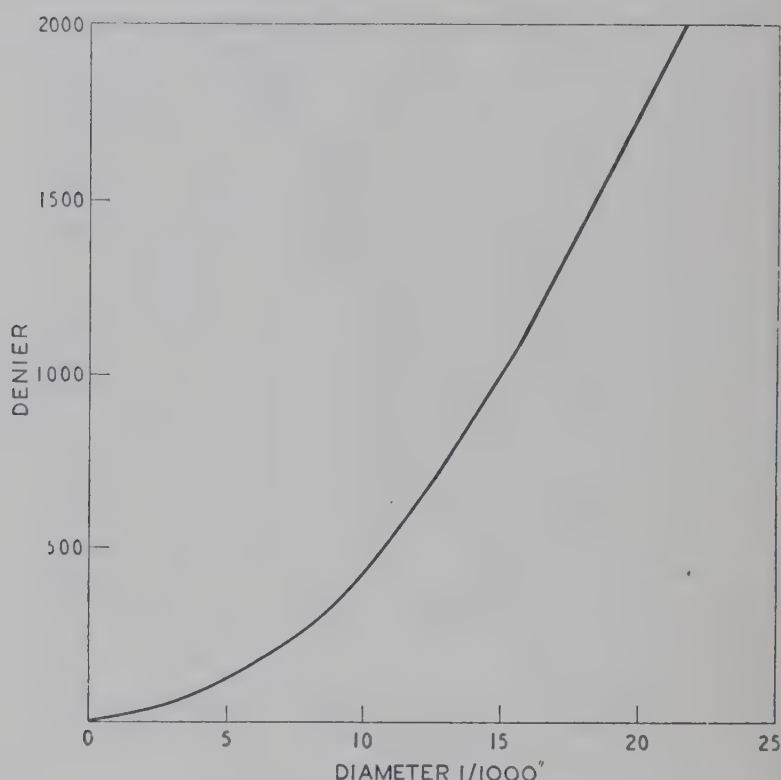


Fig. 30.1.—Diameter/denier relationship

immediately after extrusion to the force of a blast of compressed air. This floss is, however, not strictly a textile fibre although obviously related to it. Of the above textile forms it is stressed again that up to the present the only serious commercial production has been concentrated on the monofilament yarns.

The sizes of polythene monofilament yarns are basically specified by diameter measured in thousandths of an inch, although later this is often converted into the textile yarn number called denier for convenience of calculation at the cloth stage. The denier (weight in grams of 9,000 metres of yarn) is related to the square of the diameter, and is therefore more revealing in terms of variation of bulk of yarn and its likely effect on cloth regularity (see Fig. 30.1).

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Table 30.3.—EQUIVALENT DENIERS, COUNTS, AND RUNNAGE

Nominal diameter (1/1,000 in.)	Nominal denier	Nominal cotton count ^a	Nominal yards/lb
5	125	42s	35,500
7½	250	21s	18,000
8½	350	16s	13,500
10	475	12s	10,000
12	675	8s	7,000
15	1,000	5s	4,000
21½	2,000	2½	2,500

^a Cotton counts = number of hanks per lb. (1 hank is 840 yards).

As a means of accurate control in production, and routine testing thereafter, diameter measurements by micrometer or projector are adequate for the coarser monofilaments, e.g. 0.020 in., but for finer ones, e.g. 0.005 in., the weight/length method is preferred. The cross-section of the monofilaments is virtually circular, the relationship of the major to the minor axis being around 21 : 20 and therefore errors due to non-circularity may be ignored for normal routine test purposes. With multifilament yarns the denier system is invariably used to the entire exclusion of the diameter method for two main reasons. First such yarns are measured by the conventional trade system agreed and accepted by the producers and users of rayon yarns. Secondly and more important is the fact that it is not possible to use diameter accurately as a measure of multifilament yarn size in that the yarn assumes an ever changing ribbon-like form according to its path, pressure and lie at any given point. Staple fibre size is determined by measurement of the denier of the individual fibre, and length of the staple, both of which are most important to the maker of spun fibre yarn. Equivalent deniers counts and runnage are given in Table 30.3.

PROPERTIES

The general chemical and physical properties of polythene have been dealt with elsewhere*, and these obviously are the controlling factors in determining the basic properties of the textile yarns made from it. It is proposed only to deal with textile properties in this section, and to compare them with those of other fibres.

Tensile behaviour

Low density polythene yarns are modest in strength, but high in extensibility compared with other textile fibres. The strength is usually quoted in terms of grams load per denier required to break the yarn. This value

* See Chapters 9 and 10.

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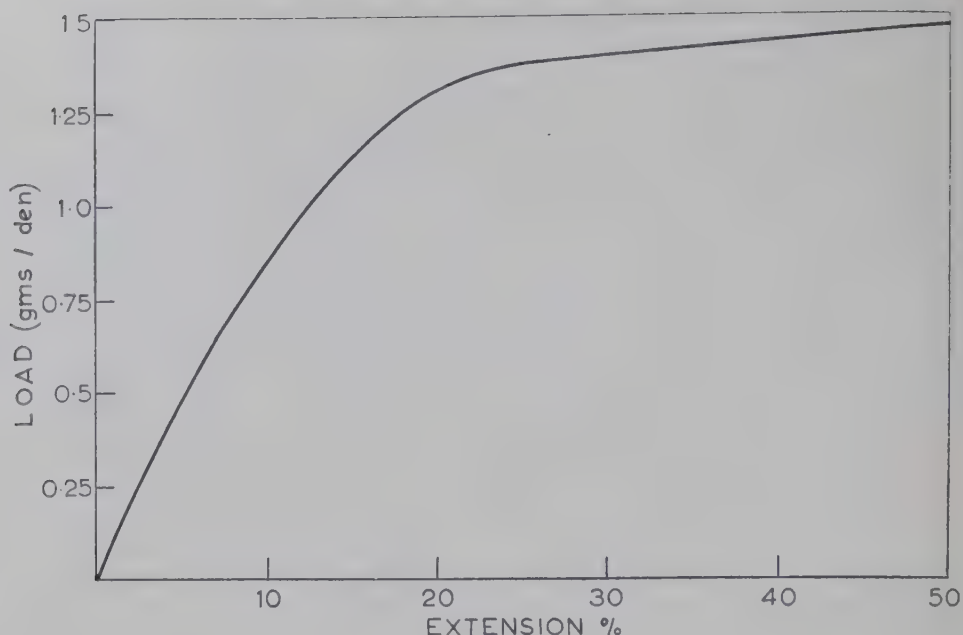


Fig. 30.2. Typical load extension curve for monofilament $8\frac{3}{4}$ diameter (Curlene)

(called the tenacity) is in the range of 1.0 to 1.5 grams/denier with corresponding extensibility from 50% to 25% according to the degree and conditions of drawing given to the yarn. The fact that wetting does not influence these properties is an advantage for polythene (compared for example with some cellulose fibres which lose up to 50% strength and gain up to 75% extensibility on wetting). The initial modulus is low compared with the general range of fibres whereas the toughness is in the middle range for textiles. An approximate indication of the values to be expected from currently produced monofilaments is given below.

Tenacity: 1.4 gm/denier.

Extensibility: 45%.

Initial modulus: 0.1 gm/denier/1% extension.

Work of rupture: 4.5 gm cm/gm.

A typical stress strain curve is shown in Fig. 30.2.

Density

This is low compared with textiles generally at approx. 0.92 gm/cc. It is the lowest true density of any normally used textile fibre (there are fibres with a lower apparent density due to air pockets inside them, e.g. kapok with apparent density of approximately 0.25 gm/cc. but the true density of the kapok fibre cellulosic substance is approximately 1.5 gm/cc.). The majority of textiles have densities in the range 1.1 to 1.7 gm/cc. There are two advantages to be found here for polythene. First is the low weight per unit bulk of material giving higher runnage in terms of yards per lb. for any given diameter compared with other textile yarns. Secondly polythene yarns or fabrics made from them will float on water.

Thermal properties

The low melting point of polythene, in the region of 110–120°C, means that it cannot be ironed with an ordinary domestic iron even at its lowest thermostat setting for rayon, which gives a soleplate temperature in this region. On the other hand this low melting point can be turned to advantage in the making of fusible interlining fabrics.

The shrinkage on heating of typical commercial drawn polythene monofilaments is shown in Table 30.4. This shrinkage can be turned to

Table 30.4.—SHRINKAGE OF DRAWN POLYTHENE FILAMENTS

Temperature °C	Approx. shrinkage, %	
	Diameter 0.005 in.	Diameter 0.010 in.
45	5	5
55	8	9
65	12	14
75	20	21
85	26	30
95	36	40
105	50	58

advantage in the making of novelty constructions of the blister cloth type but it is some disadvantage in upholstery and clothing fabrics in that these in consequence of it must be submitted to a pre-shrinking treatment to stabilize them before use.

Moisture relations

The non-wetting and non-swelling properties of polythene are a distinct advantage for several end-uses, in addition to providing easy cleaning and quick drying as associated benefits. On the other hand a disadvantage is that it is not possible to apply dyestuffs from an aqueous bath by normal textile techniques, but this can be overcome in other ways, e.g. colouring in the mass before spinning.

Effect of various agencies

The light and weathering resistance of unpigmented polythene is moderate by textile standards, enabling car seating, deck chair canvas, clothes lines, camouflage nets and so on to be made from it. These are satisfactory in use providing that the material is not subjected to prolonged exposure under tropical sunlight conditions. Insects and micro-organisms have no effect on polythene and its resistance in this respect is high by textile standards.

Miscellaneous physical properties

The electrical resistance is very high, leading to uses for polythene monofilaments in insulating cables and as fabrics in electro-chemical

work. A problem which arises with polythene yarn processing is associated with the high electro-static charges which develop, but these are overcome in several ways as discussed later. Flexibility is very high compared with other textile monofilaments. This lack of stiffness and rigidity is a strong point in enabling compact woven fabrics to be made from polythene, which are not possible or indeed more difficult to make in other textile monofilaments. The fact that the flexibility is maintained at sub-zero temperatures is also some advantage in textiles for specialized uses.

Elastic recovery properties are high by textile standards, and abrasion resistance is moderate to good in fabrics such as upholstery and clothing.

Colour fastness of monofilaments is high in textile rating and generally equal to the vat dye category. Light fastness is the most important point and a range of colours having a fastness of 6 to 8 on the S.D.C. and B.S. scale (1-8 in ascending order of merit) can be made.

The polythene monofilaments and fabrics made from them are hygienic, non-toxic, odourless and slightly waxy to the touch.

Chemical properties

The chemical inertness of polythene leads especially to its use in filters and protective fabrics. On the other hand this has made it difficult to find a satisfactory adhesive for polythene fabrics that are required to be bonded to other materials, which in turn limits their method of application in travel goods, shoes, etc.

MAKING OF FABRICS FROM POLYTHENE MONOFILAMENTS

There are several ways of converting yarns into textile fabrics and these include weaving, knitting, braiding and lacemaking. They differ from each other in the way in which the threads are caused to interlace, loop or intertwine with each other to form the structure which is called a fabric or cloth. Now it is possible technically to use any of these techniques for the making of fabrics from polythene monofilaments, but commercially the main one is weaving. This technique enables a very wide variety of textures of fabrics to be produced from monofilaments sufficient to cover the majority of the end-use requirements which have been established up to the present time.

A woven fabric comprises two sets of threads, the warp or lengthwise ones, and the weft or crosswise ones, which interlace with each other at right angles. The warp and the weft require to be mounted in the weaving loom on separate packages. The warp package is a very large bobbin or beam on to which are wound several hundred or thousand parallel threads, whereas the weft is wound single end on to pirns which are approximately 7 in. long by 1 in. diameter shaped like a short candle. The pirn fits inside the shuttle, which flies backwards and forwards through the divided warp threads to form the cloth. The preparation of warp and weft is carried out by standard textile methods when using

polythene monofilament yarns. There are, however, certain points of difference compared with normal textile yarns due to the special characteristics of polythene. First in the preparation of the warp, during the running of the large numbers of threads together at speed, high electrostatic charges are developed which cause repulsion effects disturbing the lie of the threads and also attract the dust and dirt from the atmosphere. This condition is alleviated by the use of a static eliminator usually of the high voltage electrical discharge type, placed as closely as possible to the point where the threads are laid together. Tension control on the individual ends is also very important due to the elastic and springy nature of the monofilaments. Tensions must be kept uniform and of course well below the yield point of the material, especially in that the initial modulus is on the low side compared with other textiles. The top limit for tension in winding polythene monofils is generally about 0.25 gram per denier compared with the breaking point of about 1.5 grams per denier and yield point of about 1.25 grams per denier. Another peculiar property of polythene monofil is the ease with which normal textile knots slip on it when tension is applied. Double knots are the only ones which will hold, but these are in general too bulky to pass through the reed (fine comb) in the loom, thus warps are best made knotless. This however has an economic aspect in that it now becomes necessary to ensure that the supply package contains a whole number of exact warping runs in order to avoid a high waste factor.

When the warp is made it is put straight to loom without any sizing treatment such as is normally given to textile yarns. Sizing applies a protective coating of starch, gelatine, casein or synthetic material to the yarn but polythene monofilaments by virtue of their physical form do not require (and would not accept) such protection.

With regard to the weft pirn, the preparation of this follows normal practice with attention again being focused on tension control. The method of applying it is also critical in that although polythene monofilaments are robust, sharp bends and edges must be avoided in the yarn path through the machine otherwise surface cutting, bruising or cracking may occur, especially with the coarser monofilaments. Furthermore, due to the springy nature of the monofilament wound on to the small diameter pirn, there is a tendency for it to coil off readily. Special measures are taken to prevent this during weaving and the pirn wind traverse and tension control must also be balanced to minimize it.

The above warp and pirn, and other special packages called cheeses and cones are all products of the processing department or mill which occupies an intermediate stage in the textile flowline between primary yarn producer or spinner and fabric producer or weaver.

Weaving, as has already been noted, is the interlacing of two sets of threads, and the scheme of interlacing is called the design or weave. In the case of polythene monofilament yarns the weaves used are nearly always simple geometric ones rather than ornate complex designs. The three main types of weave in use are shown in Fig. 30.3.

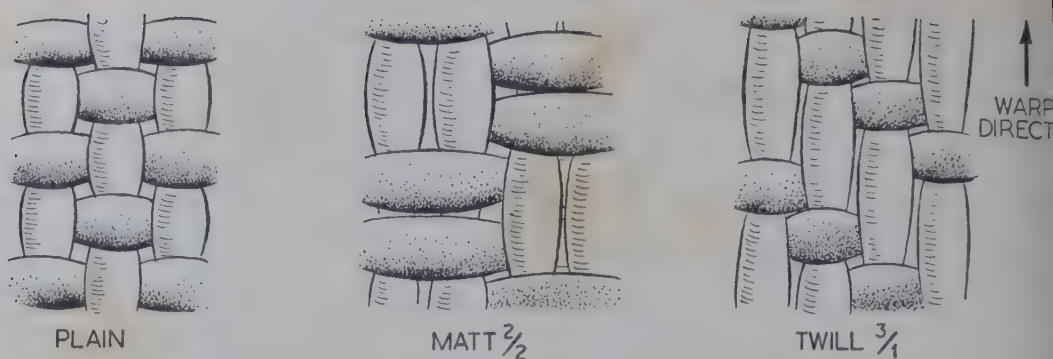


Fig. 30.3 Thread diagrams showing three typical weaves for polythene monofilaments

Plain weave is used for filter and protection cloths where an open texture of square or rectangular mesh shape is required. Matt weave is used for similar purposes and has some advantage in possessing relatively higher tearing strength. The twill type weaves enable a more compact fabric to be made, and this is favoured for overalls, industrial cloth fabrics and most upholstery cloths.

With only a little attention to small details, normal textile looms can weave polythene monofilaments satisfactorily. For example looms weaving rayon coat lining can easily weave 0.005 in. diameter monofilaments but for handling 0.020 in. diameter a much heavier type of loom such as is used for making cotton drills or canvas is preferred.

During weaving, tension control has again to be exercised with care, and electrostatic charges can cause soiling problems in certain cases. Where the latter are experienced the application of a suitable antistatic lubricant to the yarn in the warp helps to overcome them.

In planning the cloth to be woven in terms of width and length of the piece and sett of the thread spacing in terms of yarns per inch in warp and weft, due account must be taken that, during the next process of finishing the fabric, some shrinkage must inevitably take place, and allowance for this must then be made at the outset.

In the normal way the majority of ordinary textile fabrics are dyed and finished after weaving in order to bring them into a satisfactory state for selling. It has already been stated that polythene monofilaments differ from most of the other textile fibres in that, as they are not wetted or penetrated by water, normal textile methods of dyeing fail to colour them. Thus, for coloured materials, the colour is obtained by the incorporation of suitable pigments or dyes in the polythene prior to extrusion of the monofilaments and therefore there is no possibility or necessity for the ultimate fabric to be piece dyed. On the other hand some form of finishing treatment is often required for polythene monofilament fabrics and obviously this is determined by the end-use to which each particular one will eventually be put in service.

As the fabric comes from the loom, it is liable to contract and shrink when exposed to temperatures above 40 to 45°C (see "Thermal properties" above). There are some uses for the fabrics which do not involve exposure



Plate 30.1. Polythene monofilament yarn size 0.021 in. diameter.

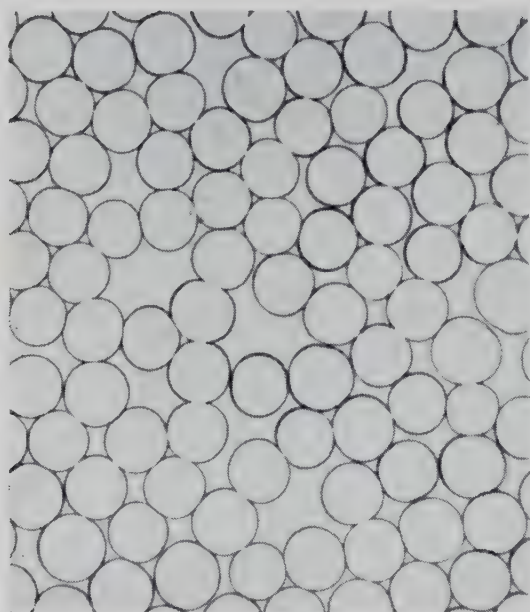
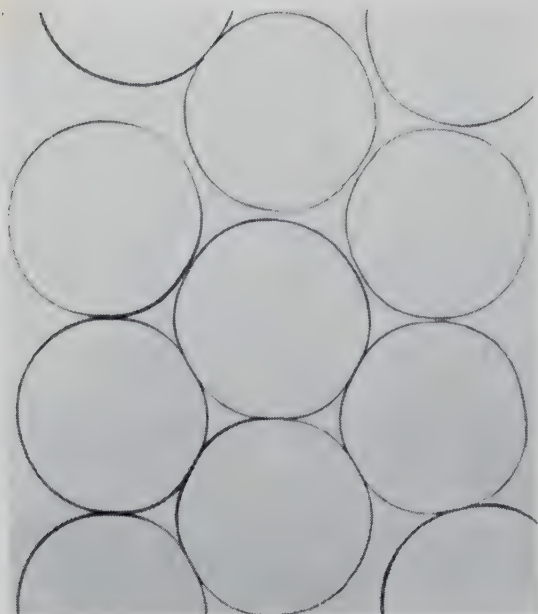


Plate 30.2. Cross sections and longitudinal views of monofil (top) and multifilament. Cross sections are almost circular in small diameters, and slightly oval in large, the ratio of major to minor axis being about 1.05:1

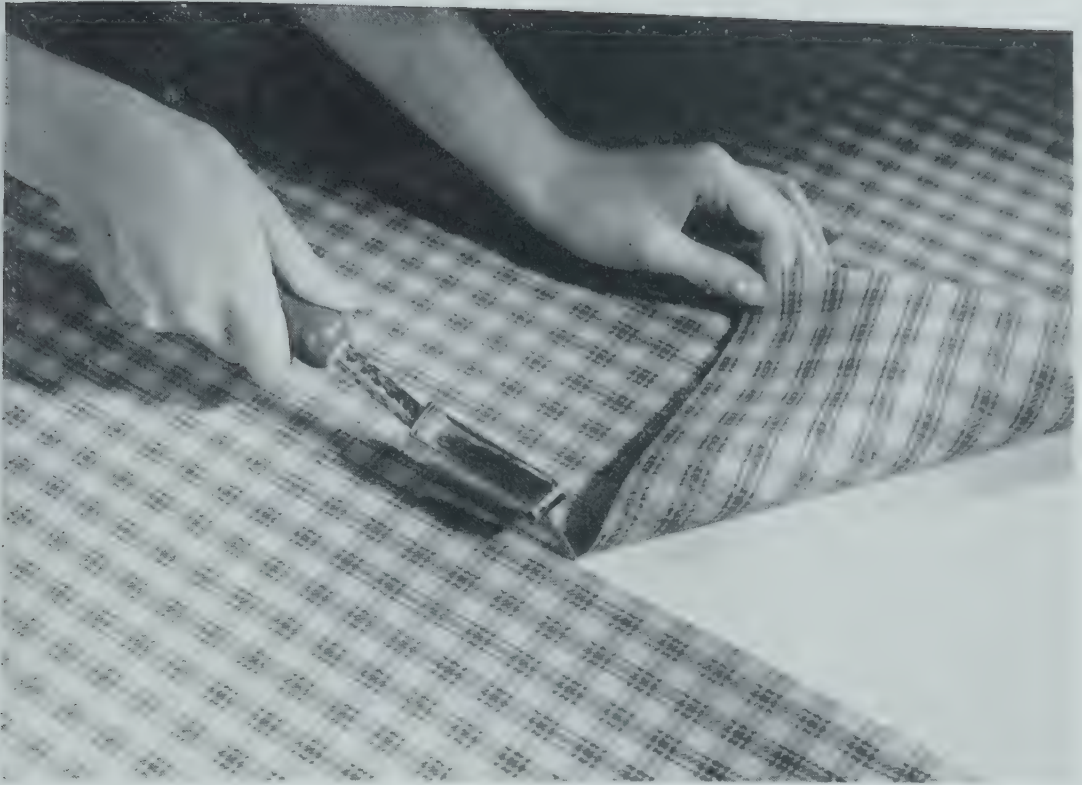


Plate 30.3. Check woven upholstery fabric made from coloured monofilament yarns of 0.010 in. diameter in twill weave. The fabric is being cut with an electrically heated knife which melts and seals the edges thereby preventing fraying

Plate 30.4. Herringbone twill weave fabric made from 0.010 in. diameter monofilament yarns in use as a trim for bus seating





Plate 30.5. Woven stripe fabric made from coloured polythene monofilaments of 0.010 in. diameter in use as deck chair seating material

Plate 30.6. Rayon fabric containing spaced threads of polythene which are shrunk by heat in finishing to promote pockets or blisters in the body of the cloth. This is called a "seersucker" effect

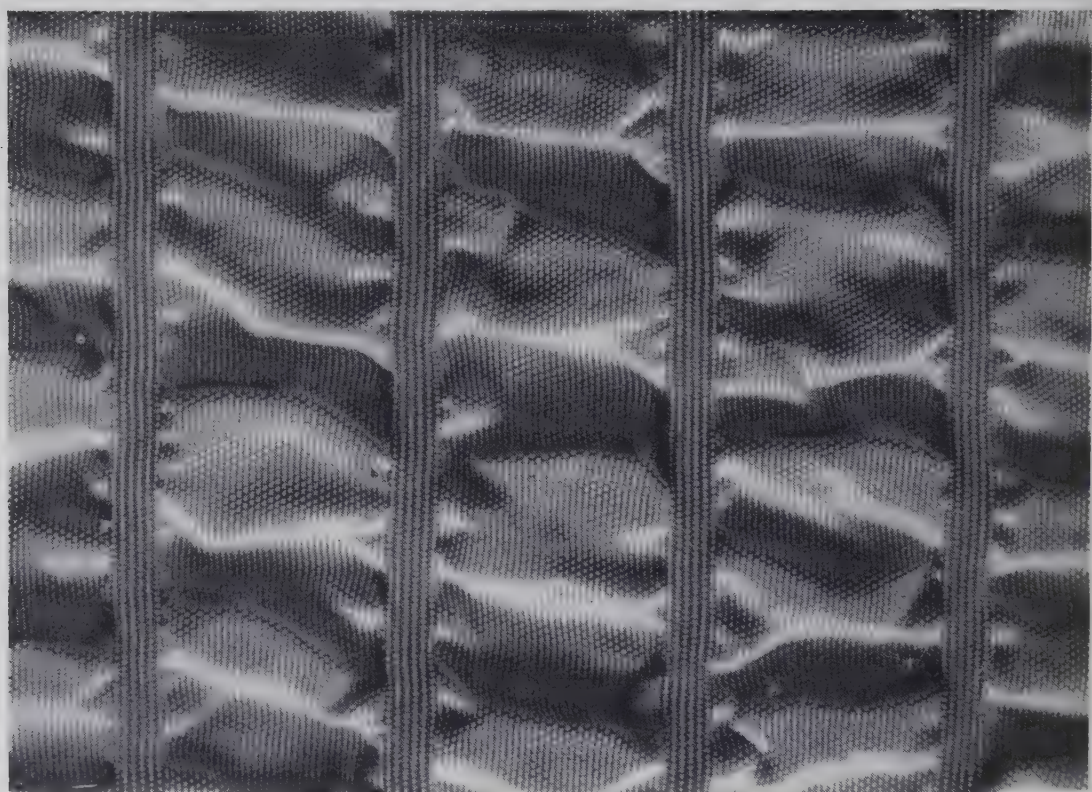




Plate 30.7. Protective overshirt woven in twill weave from 0.005 in. diameter monofilaments. The cloth has been stabilized and calendered to close the weave. The high lustre arises from this calendering effect

Plate 30.8. White laboratory overall made from twill weave fabric composed of 0.0075 in. diameter monofilament yarns. The fabric has been finished in similar manner to the shirt above.





Plate 30.9. Fused collars bonded with interlining containing polythene monofilaments. The collars are seen here as they are presented to the heated press

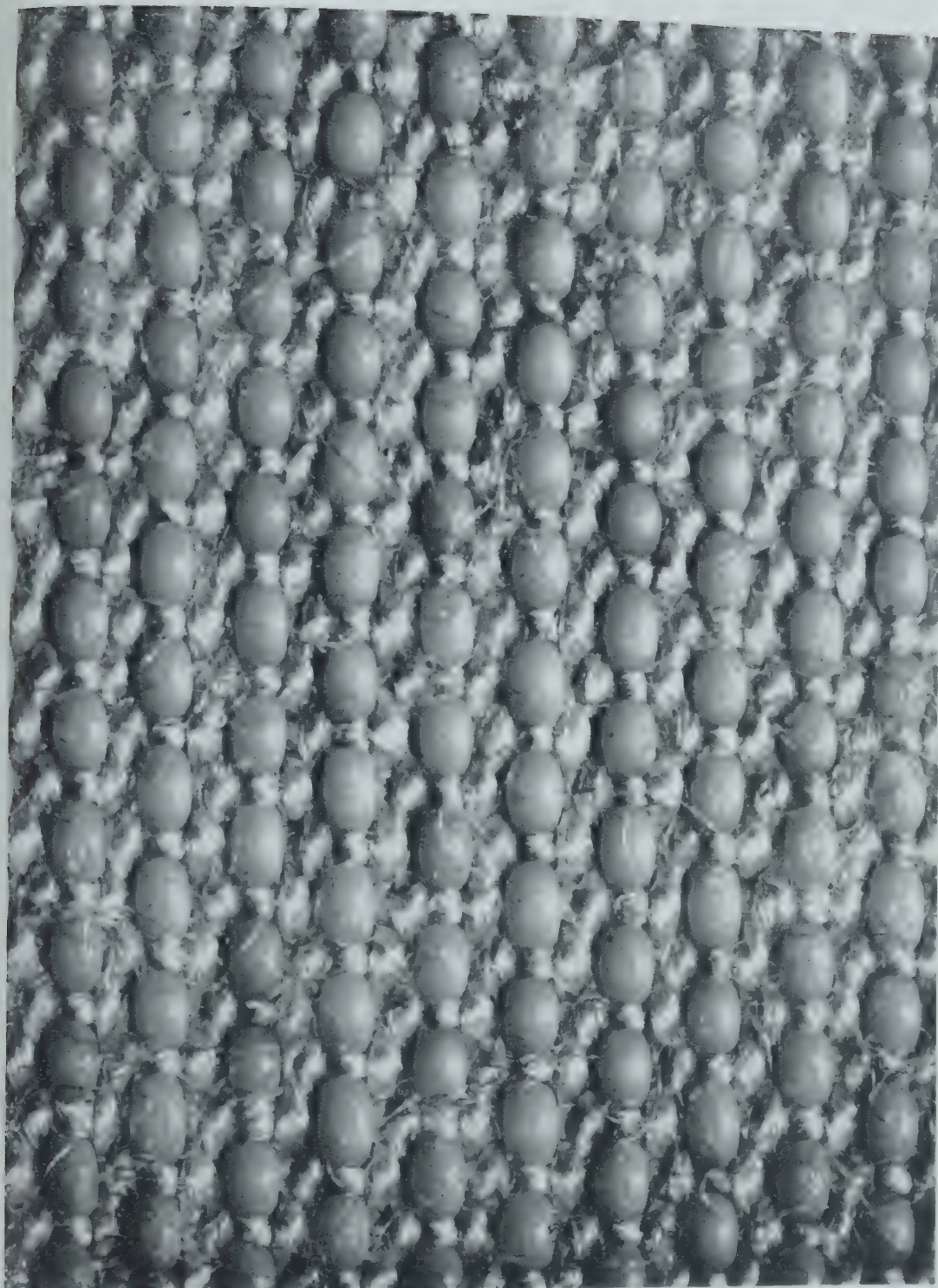
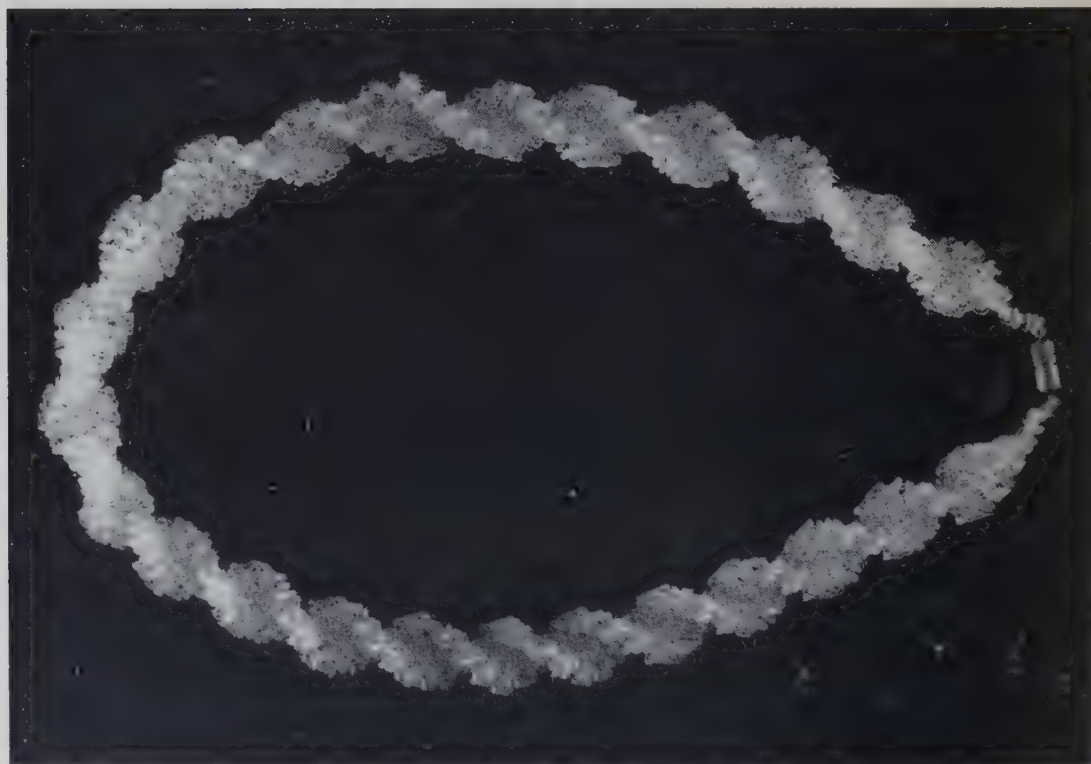


Plate 30.10. Fusible interlining of cotton and polythene. The structure of the fabric is shown considerably enlarged ($\times 16$). The fibrous cotton yarns and the polythene monofilaments (0.010 in. diameter) are clearly shown



Plate 30.11. Ropes with special physical properties can be made from polythene monofilaments. This example is composed of 0.010 in. diameter monofilaments

Plate 30.12. A novelty knitted necklet made from 0.030 in. diameter unstretched monofilaments. The unstretched material gives a soft, pearly lustre compared with the harder glitter of highly stretched monofilaments



to other than room or normal atmospheric temperature, for example, cold filtrations, protection cloths in industrial processes with no artificial heating (one instance being cake tray covers used in the viscose process), towing targets for aircraft gunnery training and so forth. Now for such uses polythene monofilament fabrics can be used in the loomstate without the need for finishing. It is obviously cheaper to use loomstate fabrics where possible thereby saving the cost of finishing and avoiding the increased cost due to area loss on shrinkage of the fabric during finishing.

Preshrinking and finishing

However if the fabric is to be used under conditions which will involve exposure to temperatures greater than 40 to 45°C then it becomes necessary to give it a stabilization treatment as part of the finishing process. This stabilization obviously involves preshrinking of the fabric by exposure to heat at a temperature a little higher than the maximum which it is liable to encounter in use. In practice it is found possible to stabilize most polythene monofilament fabrics to such a degree that they will not shrink more than 2% when exposed to heat at a temperature of 65 to 70°C in service. This result is achieved by preshrinking the material by the application of heat at a temperature of about 80°C. Higher preshrinking temperatures than 80 to 85°C would not normally be recommended for polythene monofilament fabrics as under such conditions the shrinkage force becomes very severe and difficult to control with textile satisfaction.

The process of preshrinking can be carried out by any convenient method of uniformly applying controlled heat to fabric, and several techniques for doing this have been worked out for the various type of equipment to be found in the normal textile piece goods dyehouse. These involve the use of hot water, hot air, or heated cylinders, in jigger, stenter or can drying machines. In the processes which involve the use of hot water, the excess water which clings to the fabric, and remains in the interstices of the weave by capillarity, must be removed afterwards. This may be done by suction drying rather than by the application of further heat. In all the techniques mentioned the temperature must be carefully controlled, be it that of the water, air or surface of the cans. It is also very important to give the fabric freedom to contract, in that if it is held under tension lengthwise during the run it may not relax fully to the stable state, and it will then exhibit a greater heat shrinkage potential than was forecast from the temperature conditions of preshrinking. So far in this discussion the merits of preshrinking to give stability only have been extolled. There are however other virtues in the process mainly concerned with increasing the toughness and durability of the ultimate fabric. There are three contributory reasons for this. First the shrinkage effect results in the fabric becoming more compact, with threads per inch increased resulting in heavier weight per unit area. Secondly the extensibility of the fabric increases and this is reflected in higher work of rupture and increased resistance to tearing

forces. Finally surface cracks which appear in the skin of the monofilaments when they are caused to form small curves or bends, such as occur at every interlacing in the weave, are healed and disappear on being subjected to the heat contraction treatment.

The fabric in the stabilized form may now be used for the purpose intended, or it may experience a final process to consolidate it yet further and give a surface lustre with a degree of flattening. This is achieved by subjecting it to a pressing, calendering or mangling process. In the case of upholstery fabrics for car seat covers, bar stools, etc., a calendering finish improves the lustre and appearance of the material. With protective overall and clothing fabrics on the other hand the same process of calendering is used to close the interstices of the weave and thereby reduce the porosity. This is done to combat penetration by splashed liquids, rather than to enhance the appearance, which although it also occurs is a secondary consideration in this particular instance.

Making up

The fabric thus suitably finished can now be made-up into bags, packs, garments and so forth, using normal equipment without encountering any special problems. The cutting out of fabrics made from polythene yarns can be done very effectively with electrically heated knives which give an edge which is sealed over by fusing together the cut ends of the yarns at the time the cut is made. Such an edge which does not fray is adequate for some industrial purposes without the need for further hemming. Where sewing is required this again is a normal straightforward operation. In sewing it is best to use a rounded point needle rather than a sharp one with monofilament fabrics, as the rounded one tends to push the monofilaments apart rather than to pierce, weaken and tear them. Normal sewing threads are satisfactory for many purposes including upholstery, but in the case of protective clothing to be used in chemical processes, the sewing thread must obviously have chemical resistance similar to the polythene fabric composing the body of the garment. Polythene yarns by virtue of their low initial modulus and elastic, rubbery characteristics are not suitable for the doubling of sewing threads. Therefore where the need arises other sewing threads made from synthetic polymer bases are best used.

THE USES OF POLYTHENE TEXTILE YARNS AND FABRICS

The uses and limitations of polythene monofilament fabrics can be predicted in general terms from the properties of the base material. The special feature of its low melting point implies that it cannot be used in the usual run of dress fabrics which are to be hot ironed or hot pressed. On the other hand this same thermal characteristic can be turned to advantage in the making of fusible interlinings for bonding purposes.

First then in that large part of the textile fabric business called the dress trade it is obvious that fabrics made from or containing polythene

yarns must play only a limited part. The important reason for this has been given above and in addition there are two further points which limit its flexibility in this direction. First there are the small number of fabric textures which it is possible to get with monofilaments and secondly the inability of the fabric to be ornamented by dyeing and printing in the normal textile manner.

Despite these disadvantages, however, there is one group of woven textiles used in the dress goods trade for which polythene yarn is very suitable. This group includes the seersucker and blister cloths.

This type of cloth is woven from normal spun or filament textile yarns but it also incorporates a few threads of polythene yarn spaced at intervals in the piece. The fabric is woven flat, but when it is later subjected to the influence of heat in finishing the polythene yarns shrink whereas the other normal textile yarns remain stable and virtually unaffected. Thereupon the localized tight and slack places in the cloth create the puckered effect which is the predominant characteristic of such fabrics. This texture of fabric is never normally ironed because to flatten it would obviously spoil its appearance, and therefore no significant hazard exists relative to the use of polythene yarn in this end-use.

In upholstery fabrics, polythene monofilaments of 0.010 in. to 0.020 in. diameter make very attractive seat covers when woven in gay multi-colour checks. Similar fabrics but with stripes of colour are suitable for deck chairs. In addition to the attractive appearance the ability of the fabric to wipe down easily for cleaning, its flexibility, non-wetting, toughness and good wearing properties all contribute to making polythene suitable for this end-use. Continuing in the realm of domestic fabrics, lightweight plain woven coloured checks of the gingham type made from 0.005 in. diameter polythene monofilaments are both attractive and utilitarian in bathroom and shower curtains. They possess good colour, appearance, hang or drape, and also remain unaffected by water or steam in the atmosphere. The fabrics are of course stabilized in finishing after weaving and, particularly in the case of the shower curtain material, calendering to reduce the porosity is desirable. The cleaning of such curtainings is a very simple matter compared with the ordinary domestic wash. It is only necessary to steep them in cold or lukewarm water plus detergent, rinse and air-dry naturally to remove the surplus clinging water droplets from the interstices. No ironing is necessary (nor indeed possible) because of the remarkable crease resistance of polythene textile yarns.

Probably the most interesting application of the special properties of polythene in textiles is in the making of fusible interlining fabrics for bonding in the manufacture of semi-stiff collars, cuffs, lapels and so forth. It has long been the custom to use interlinings in the various built-up parts of clothing which need to have a degree of stiffness and body, yet remain sufficiently flexible to be comfortable and adaptable to the movements of the wearer. In the cases of collars the interlining is in the form of a relatively coarse woven cotton fabric and this is sandwiched

between the two facing pieces of finer quality poplin or other shirt material. This construction gives a soft collar, and the semi-stiff type achieved by bonding the interlining in some way to the facing cloth to form a three layer laminate. One standard method of producing permanent result involves the use of a thermoplastic bonding agent in conjunction with the interlining so that on softening the thermoplastic material with a solvent then applying heat and pressure to the made-up collar the whole is bonded together into one piece. The usual way of introducing the thermoplastic material into the structure is to incorporate it as a spaced yarn in the interlining cloth. Polythene monofilament is a very satisfactory fusing component which has the advantage that no solvent is required during the bonding operation. It is used in the following way. The interlining structure is arranged in weaving so that in the warp one thread in every three is polythene monofilament and the other two are cotton. The weft is all cotton so that the fusing medium appears in one direction only for reasons of ease of technical control in weaving. The sizes of the monofilaments used are 0.0075 in. to 0.010 in. according to weight of interlining required and the colour is generally white since this is of optimum general utility in catering for white, plain colour and striped shirtings. During the weaving operation it is arranged that the polythene monofilament warp threads are fed into the cloth at a faster rate than the cotton warp threads so that the loops or weave floats of the polythene monofilament stand proud of the cotton surface of the interlining fabric. There are two reasons for this: first in order to give good positioning of the polythene monofilament for later fusing and bonding (like a series of spot weld points) and secondly to allow for the differential shrinkage of polythene and cotton warp yarns in finishing. After weaving the cloth is scoured and piece bleached in order to remove starch size and impurities from the cotton, and to give the cotton the full white appearance which is necessary in interlinings. The whiteness of the bleached cotton is generally reinforced by the addition of optical bleaching agents. Finally the fabric is dried to remove water from the cotton parts (the fabric is approximately half cotton, half polythene by weight) and finished to width. Throughout the whole process great care is taken in controlling temperature so that the shrinkage of the polythene monofilament component of the cloth is kept within bounds, and to ensure that it is not damaged or melted prematurely.

This finished interlining is now used in the middle of the collar as already mentioned, then the made-up article is bonded under pressure at approximately 150°C for 15–18 seconds each side. The laminate is thus formed and after a little surface treatment is ready for use. The advantages of polythene over other materials used for this purpose are the simplicity of the operation, the lack of troubles associated with plasticizers and solvents which are not needed with polythene, and the high performance of the bond in wear and wash. The bond is reinforced whenever the collar is hot ironed after washing and by the nature of the elastic

polythene bond layer is particularly free from point curling to which many ordinary semi-stiff collars are prone after a short time of wear. Furthermore interlinings containing polythene yarn as the fusing medium have been successful with synthetic fibre shirtings of the nylon and Terylene types which do not respond so well to some of the methods of bonding with other interlinings.

The exceptionally high resistance of polythene to attack by chemicals enables it to be used in cloths intended for filtration, screening, protection and overalls in industrial chemical processes. The main proviso is that the processes must operate within the capabilities of the polythene in respect of temperature. A range of such cloths are made in monofilaments from 0.005 in. and even 0.020 in. diameter.

With respect to the use of polythene yarns in protective industrial overalls and clothing, the unique point is that by virtue of the remarkable flexibility of polythene, cloths which are suitable for the purpose can be woven from monofilaments. The majority of textile monofilaments are far too rigid to be used for this same purpose in equivalent diameters to those used in polythene. One example of the success of polythene in this connection is a shirting twill woven from 0.005 in. diameter monofilaments in warp and weft which is used to make protective overshirts for viscose spinners and chemical process workers who are in contact with acids. This monofilament is equivalent to 120 denier and it is very doubtful if any other textile monofilament could be used in equivalent size in such a fabric and yet give the required flexibility in the cloth. For chemist's laboratory coats, works overalls and boiler suit types of clothing, a heavier fabric than the shirting is needed and this should be a similar weight to the denim and florentine drill. This is achieved by using 0.0075 in. diameter monofilaments, again in a twill weave. These 0.0075 in. diameter monofils are approximately 250 denier which is about double the denier of the 0.005 in. diameter monofilament and therefore the cloth approaches double the weight per unit area in similar construction. After weaving these cloths, they are stabilized and calendered by the methods previously described under finishing processes. The stabilizing treatment, in addition to limiting subsequent shrinkage on washing, also helps to reduce the porosity by contracting and consolidating the structure. The flattening effect resulting from the calendering process assists still further to reduce the porosity of the cloth. Now, it is neither desirable nor sensible to endeavour to return woven monofilament fabric to a continuous impervious sheet form. The merits of the woven monofilament structure lie in its flexibility, directional stability, higher tearing strength, and porosity, compared with a continuous sheet of the same material. The last mentioned plastics sheeting is obviously better for complete protection from liquid splashing but it is not comfortable or healthy to wear continuously throughout a daily shift on the plant. A fabric which can breathe through its interstices as is the case with woven polythene monofilaments can be worn with adequate comfort throughout a shift at work. Thus although the heat

contraction and calendering treatments are used to reduce the porosity of the fabric it is not desired to lose this altogether. The result then is a controlled compromise which gives reasonable comfort with an adequate measure of first protection from chemical splashes.

There are many other uses for polythene monofilament in textiles of which the following are but a few. Towing targets for aircraft gunner training are made in banner form from a woven cloth made from 0.002 in. diameter monofilament in a coarse leno texture. The toughness, low density, flexibility, elastic properties, non-wetting and low temperature flexibility of polythene all have some bearing on its application to this end use. Shoe fabrics can be most attractive in polythene and, because of its non-toxicity, uses in surgery and food industries have been established. Specialized ropes can be made from polythene monofilaments and these are non-wetting, able to float on water, and flexible at low temperature, besides of course possessing the usual high resistance to chemicals. A most attractive domestic clothes line can be made from 0.050 in. diameter monofilaments and this possesses the usual merits of polythene in addition to which it is easily cleaned and not subject to attack by micro-organisms which eventually have some degrading influence on most other textiles used for this purpose.

CURRENT AND FUTURE DEVELOPMENTS

This chapter has so far dealt with the low density types of polythene yarns commercially available in bulk quantity during recent years. The technique of yarn manufacture is, of course, being improved and extended, but the greatest improvements are now to be associated with the development of higher density polythenes.

These type of polythene enable a much stronger, tougher, more durable yarn to be produced. Compared with a tenacity of 1 to $1\frac{1}{2}$ grams/denier for low density polythene it is now possible to produce yarns within the 4-6 grams/denier range. The stronger yarns have rather lower extensibility, more rigidity, higher thermal stability and melting point than the low density types. Table 30.5 shows some of the properties of a commercial example (Curlene X.3) of yarn from high density polythene. All these altered characteristics can be exploited to advantage in textiles. First, the great improvement in tenacity enables an existing construction of material to be considerably strengthened, giving a strength comparable with nylon and Terylene. Alternatively, maintaining the same overall strength characteristics the structure can be lightened in weight by using either a more open texture in place of or combined with finer diameter yarns. The greater thermal stability permits a reduction in the severity of the stabilization treatment, resulting in less shrinkage. The fact that the material dimensions are less sensitive to temperature increase may eliminate the need for stabilization in finishing some types of cloth. On the other hand, providing that due allowance for shrinkage is made in the construction calculations cloth can be produced dimensionally stable to boiling water.

TEXTILE YARNS AND FABRICS

Table 30.5.—PROPERTIES OF YARN (COURLENE X.3) FROM HIGH DENSITY POLYTHENE

Mechanical properties	<p>Tenacity Extensibility</p> <p>Wetting</p> <p>Toughness Density</p> <p>Elastic recovery</p> <p>Abrasion resistance</p>	<p>4 to 6 grams/denier 40 to 20 %. (Extensibility and tenacity are interdependent, the higher tenacity being associated with lower extensibility and vice versa)</p> <p>This has no effect of mechanical properties</p> <p>Excellent by textile standards</p> <p>At normal temperatures approx. 0.96 gm/cc.</p> <p>Very good—complete up to approx. 70% of breaking load</p> <p>Excellent. Much improved on normal (low density) polythene yarns and approaching that of polyamides</p>
Thermal properties	<p>Softening point</p> <p>Melting point</p> <p>Heat shrinkage</p>	<p>120°C approx.</p> <p>135°C approx.</p> <p>At 60°, 3 to 4%</p> <p>At 100°, 10 to 14%</p>
<p>Chemical resistance</p> <p>Electrical properties</p> <p>Moisture relations</p>	<p>} Similar to normal (low density) polythene yarns</p>	

ACKNOWLEDGEMENT

Acknowledgment is made to the directors of Courtaulds Limited for permission to publish this chapter, and also to all colleagues who have assisted in supplying data for its preparation. Courlene and Courlene X.3, referred to in this chapter, are registered trade names of Courtaulds Limited.

CHAPTER 31

FUTURE OUTLOOK IN THE U.K.

A. RENFREW

TODAY the demand for polythene is growing even more rapidly than that for the two other big tonnage plastics, polyvinyl chloride and polystyrene, and in a few years' time polythene may well be the biggest tonnage plastic in the world. In 1965 the world demand for polythene may exceed $1\frac{1}{2}$ million tons a year: this figure includes the original low density types made at high pressures and the new higher density types made at either low or high pressures, but not copolymers and chemical derivatives. When the high density polythenes were first produced commercially some authorities expected that they would displace the low density polythenes entirely. Events have shown that there was no basis whatever for this point of view and new high pressure plants to produce low density polythenes are being erected in many parts of the world. High density materials are, however, extremely important and perhaps 40% of the total market in 1965 will be met by these relatively new materials. The polymers with densities of about 0.96 are so different from low density polythenes that they can almost be considered as a different group of plastics which, like other new types of plastics, will find new markets.

RESEARCH

There is still a great deal to be learned about the reaction kinetics of ethylene polymerization and with increased knowledge greater control of the reaction will be possible.

The effect of chain branching and, in particular, the effect of long and short chain branching and of the distribution of the branches along the chain, is being studied and important results can be expected. The technique of electron bombardment (see Chapter 13) has given us a useful method of estimating the length of branches by analysis of the gases evolved during the bombardment. It is likely that long branches are formed by a bimolecular reaction which will depend on temperature as well as on concentration. As more information is accumulated, closer control of the structure, and therefore the properties, of the polymers should be possible. There is a very real chance that out of fundamental studies will come materials with new properties, e.g., clarity in thick sections, transparency with complete freedom from film blocking, and stiffness with high elongation at break.

The revolution in polymer chemistry, triggered by Ziegler's¹ and Natta's² work on surface catalysts, will result not only in the manufacture

of high density polymers at low pressures, but also in the interpolymerization of ethylene with other hydrocarbons under conditions of isotactic polymerization. By themselves, isotactic polyhydrocarbons have been shown to differ in properties from the corresponding amorphous polymers. e.g. isotactic polypropylene has a softening range between 160 and 170°C and isotactic polyvinyl benzene softens above 200°C. Copolymers with ethylene should clearly have interesting properties.

There are, of course, other methods of making copolymers and polymerization will certainly be one of the components. Of the techniques now available for making graft and block copolymers, perhaps those involving chain transfer between growing chains and polymer chains³ and those involving direct scission, e.g. by rapidly shearing polymer chains in the presence of a monomer,⁴ hold out the greatest hope. One of the most interesting possibilities is the manufacture of block copolymers with the second component in the amorphous phase.

Copolymers of ethylene with other aliphatic hydrocarbons are likely to be made at low or ordinary pressures using surface catalysts. Such copolymers can, however, be made by the high pressure process but so far, the second components have not been molecularly symmetric and the main effect has been to decrease crystallinity with a consequent increase in transparency and rubberiness.

Completely different types of catalyst have been suggested and in the future may be important, e.g. gamma rays.⁵

A $(CH_2)_n$ polymer can be made by decomposing diazomethane (Chapter 1), but the process is not likely to be commercialized. This route, however, is of great theoretical interest since it permits the synthesis of completely unbranched polymers described⁶ in 1900 as polyethylene. The authors described the product as a "white, very voluminous flocculate precipitate which was dissolved in boiling cumol and precipitated by petroleum ether. In the dry state the white amorphous powder looked like chalk and was almost insoluble in all the usual organic solvents. The best solvents were boiling cumol and boiling pyridine. The melting point was 128°C."

One of the big attractions of this method is that by selecting the appropriate diazo compounds, branched polymers of known structure can be prepared. More knowledge of these polymers will assist in the synthesis of low pressure ethylene polymers of predetermined properties.

It is worth remembering that neither the high pressure nor the low pressure polymerization process would have been discovered if research workers had not been equipped to recognize and follow up fortunate accidents. Perhaps the next big advances in ethylene polymerization will come in the same way.

RAW MATERIALS

The source of the ethylene in the polymer first manufactured in the U.K. was alcohol, but today in the U.K. and in most countries ethylene is obtained by cracking oil or natural gas. However, where alcohol

FUTURE OUTLOOK IN THE U.K.

cheap and plentiful, the original route is still economic. Two new high pressure plants, one in India and the other in Australia, will, to begin with at any rate, use alcohol as a raw material. Coke oven gas has been used as a source of ethylene, e.g. in France.

MANUFACTURE

No details have been published of any manufacturing processes. Tubular reactors are known to be used in at least one of the high pressure processes, all of which are, of course, continuous as, indeed, will be some of the low pressure processes now being developed.

If the estimate, that in 1965 40% of the total demand will be for high density polythene, is true there will probably be more low pressure plants than high pressure plants in existence in that year since the average output of the low pressure plants may well be low because they will be installed where capacity does not justify the installation of a high pressure unit. Both types of plant will no doubt be capable of making polymer of any required density but, as has already been indicated, copolymers of ethylene with aliphatic hydrocarbons will probably be made in low rather than high pressure plants. These plants will probably also be best suited for the manufacture of very high molecular weight infusible polythene.

Improvements are likely in methods of hot processing polythene and of compounding it with other ingredients such as pigments, antioxidants, antistatic agents, antiblocking agents and slip agents. Internal mixers, now generally used, give excellent results but are not continuous and deliver the homogenized or compounded polythene in large lumps which have subsequently to be reduced to a powder either by sheeting and cutting or by extrusion and cutting. Extruders have not so far given completely satisfactory results in all types of mixing, but will be used extensively in the future now that the importance of screw design and of mixing devices are realized.

PRODUCTION CAPACITY

Any figures for the present and projected world capacity for polythene will be outdated as soon as printed but Table 31.1 is the situation as it appears in 1956.

During World War II polythene was manufactured only in the U.K. and U.S.A. So far there is no definite information about developments in the U.S.S.R., but the existence of some manufacturing capacity can be deduced from a recent publication.⁷ Russian representatives were shown around British polythene plants during World War II but it is not known what use they made of the information obtained. There is no doubt that polythene will ultimately be made in all industrial countries and exports from highly industrialized countries will be in speciality products.

PROCESSING

The processing of polythene consists simply in shaping the hot melt. In future, more attention will be paid to the melt history. The work

POLYTHENE

Table 31.1. PROJECTED WORLD POLYTHENE CAPACITY

	Long tons	Date
Australia Imperial Chemical Industries of Australia & New Zealand	3,300	1958
Brazil Union Carbide Elchor	2,000 4,000	early 1957 1959
Canada Canadian Industries Ltd. Union Carbide Dow	10,000 Capacity not known	1957? 1957 ?
France Éthylène Plastique Pechiney Rhone Poulenc/Kuhlmann Éthylène Plastique/Aire Liquide/Pe- chiney Huiles Goudrons et Dérivés Aire Liquide/Huiles Goudrons et Dérivés	8,000 6,000 10,000 Capacity not known	late 1956 after 1957 ? ? ?
Germany Badische Anilin und Soda Fabrik Rheinische Olefinwerke Farbwerke Hoechst Kohle Oel Chemie Chemische Werke Hüls Hibernia Ruhrchemie/Rheinpreussen	5,000 12,000 15,000 24,000 12,000 1,000 Capacity not known	Now working " " " " 1956-57 1957 1958? ? ?
Holland Dutch State Mines	5,000	end 1957
India Alkali & Chemical Corpn. of India National Carbon	about 6,500	? ?
Italy Montecatini Solvay	12,000 Capacity not known	1958? ? ?
Japan Sumitomo Mitsui Furukawa Showa Denko	5,000 12,000 3,600 7,500	1958? late 1957 1960? 1960?
Spain Unquinesa Electroquímica de Flix	6,000 Capacity not known	? ? ?
U.K. Imperial Chemical Industries Monsanto Union Carbide Petrochemicals British Hydrocarbon Chemicals	90,000 10,000 11,300 1,000 11,000	1959 ? 1957 1957 ?
U.S.A.	358,000	(See Chapter 32)
Grand total—approximately	700,000	

done on the material whilst hot and the rate and conditions of crystallization affect the properties of the final product, particularly when it is in film form. When some polymers are hot processed they become unsuitable for film manufacture because of a great tendency to block. No doubt this tendency to block is a surface effect but it is one which is effected by the melt history of the polymer.

Developments in processing machinery have been discussed in the appropriate chapters of the book and there is little that can be usefully added. The only really outstanding development which has not been discussed at length is the possible increase in speed of screws in extrusion machines.⁸ At present the screw speed rarely exceeds a few hundred rev/min but several manufacturers are experimenting with extrusion machines in which the screw revolves at several thousand rev/min with, of course, increased output. Methods of increasing output are most urgently needed: at present extrusion rates are much lower than those in the metal industry. Opinions still differ about the merits of adiabatic extrusion and some authorities prefer extruders with short barrels fed with hot polythene. Compression ratio is another important variable; at present 3 is a common figure but the trend is upwards to about 5.

Film is usually extruded by the tubular process but there may, in the next few years, be a swing towards the older flat film extrusion process since output is high and automatic machinery for fabricating the product is now available. Flat film is at present cooled by extrusion into water but air cooling may be used in future because water is not only apt to cause uneven shrinkage but also tends to impair the efficacy of agents added to film.

There are no really new processes for fabricating polythene; two of them, extrusion moulding and centrifugal casting, are little known and have not, so far, had much commercial success. Extrusion moulding was used during the war for the experimental manufacture of polythene submarine battery boxes with walls about 1 in. thick. The technique consists of coupling up a simple brass mould to an extruder and pumping hot polythene into the mould which is then cooled progressively. If really massive articles are ever required in polythene, and this is by no means an impossibility, the extrusion moulding process may be revived. Centrifugal casting has been described in Chapter 20. It is clearly suited for the manufacture of symmetrical articles other than tube, but so far no important applications, other than large bore drain pipes, have been turned out. Large articles of uniform wall thickness were shown at the Hanover Fair in 1956 and were said to be made by the new technique, details of which have not yet been published.⁹ It would appear to be some variation of the flow casting technique for which low molecular weight polythene was once used on an experimental scale. In the Engel process low density polythene of melt flow index 20 has given good results.

PROPERTIES

The properties of polymers over the density range 0.92 to 0.96 can be set out in many ways. In Table 31.2 an attempt is made to show where

POLYTHENE

Table 31.2. RANGE OF DENSITY AND PHYSICAL PROPERTIES

Density	Linear polythene, polymethylene high density polythene						
	0.91	0.92	0.93	0.94	0.95	0.96	0.97
		Original poly- thene, Alka- thene		Hostalen Super- Dylan & Hyfax, made by the Ziegler process and Alkathene HD made by the high pres- sure process		Marlex 50 made by the Phillips pro- cess and Mannesman polythene made by the Ziegler pro- cess	
Over the range of densities the polythenes increase in							
Crystallinity			%		Density 0.92	Density 0.96	
Softening point			°C		60	to 90	
Tensile strength			lb/sq.in.		110	to 130	
Stiffness modulus			lb/sq.in.		2,000	to 5,000	
					2×10^4	to 10×10^4	
And decrease in					Density 0.92	Density 0.96	
Elongation at break			%		700	20	
Impact strength			ft. lb/inch of notch		>15	1	
Moisture vapour permeability			gm/m ² /day/thou.		17	6	

today's polythenes fit into the picture. The properties do not always improve with increasing density: the extremes are given.

Polythene can be oxidized readily and precautions to prevent it are taken either by the manufacturer or by the fabricator. Methods have been devised for oxidizing polythene during extrusion and moulding or by heating the finished article. None, however, has proved commercially important and there seems little chance of future development in this direction.

APPLICATIONS

Polythene was first used to replace gutta percha in submarine cables and most of the present applications of polythene were foreshadowed in 1850.¹⁰ Gutta percha was not, of course, used for film on account of its colour, but found important applications for cold water piping and domestic utensils.

The most obvious trend in injection moulding polythene is the increase in size of the articles. The use of high density polythene suggests that mouldings from the materials may compete with high impact polystyrene. Amongst suggested new applications are car wings, bumpers, mudguards; telephones; corrugated sheet; trays; prostheses of various kinds including dentures; gears; battery cases; and, perhaps, most of important of all, food containers which can be sterilized.

A great deal has been said in literature about the great future for polythene tube, but in the last few years progress has slowed down,

perhaps because much inferior tube has been marketed in which the carbon black has been badly distributed. Blue tube has even made its appearance in some markets. The advantages of high density polythene for tube have been well publicized but its disadvantages have not been adequately stressed. The outstanding problems are oxidation at high temperature, jointing, and shock brittleness. One very important use for high density polythene is the manufacture of large bore tubes; hitherto it has been impracticable to use them because of the undue thickness of wall required for adequate stiffness.

Film has been more and more used in agriculture and one of the recent developments likely to be of considerable importance is the double wall polythene greenhouse. High temperatures can be maintained even without internal heating. In existing greenhouses an internal polythene film placed behind the glass sheets has proved very effective and has been said to pay for its installation in a few weeks.

Little is yet known about applications for sintered very high molecular weight polythene. A few articles were shown at the Düsseldorf Exhibition in the Autumn of 1955,¹¹ amongst them a picker hammer which had outlasted a buffalo hide picker hammer, a most remarkable achievement. Sintering is, however, a slow process and in the past has been used only where other processes were impracticable. Unless sintered polythene articles have outstandingly different properties from articles made by injection moulding of high or low density polythene, it is doubtful if they will be very widely used.

It is remarkable that since polythene has been discovered it has found few applications as a minor component of mixtures. Today in the University of Alberta mixtures of asphalt and polythene for road surfacing compositions, to withstand low temperatures, are being studied. If the development is successful a very big market indeed would open up. Even more important is the work going on today on the mixtures of polythene with natural and synthetic rubber. It is claimed that polythene has a reinforcing action on rubber and that mixtures might even be used for tyres.

For many years it was thought that polythene compositions could not be calendered commercially. This is no longer true of modern calenders. Table cloths are already in the market and are proving successful: other applications will follow and calendered polythene may replace calendered polyvinyl chloride compounds for some applications.

The future of polythene in the cable industry is encouraging. For many years polythene 15 kV power cable has been successfully used and, since it is cheap and easy to instal, a bright future seems assured. High density polythene is of great interest to the cable industry since the wall thickness may be reduced and toughness increased at the same time. In power cable, high density polythene may be of interest because of its high softening point but there are many other problems and progress will be slow. The improved mechanical properties of high density polythene suggests that they can be expanded to a greater extent than

low density polythene and thought is being given to expanded polythene as a substitute for paper in cable insulation.

Nothing has so far been said about polythene fibres. In the U.S.A. prospects are only moderate since even high density polythene has a low softening point for a textile fibre and retains the waxy character of the low density material.

The uses of finely divided polythene powder have been described in Chapters 23 and 24. Polythene pastes are not being tried for other applications but, as with the powder, the coating must be fused and possibly even calendered. Developments may be important but are unlikely to be big.

New types of polythene will be more suited for vacuum forming and low density polythene and new markets for thin sheets will open up.

One of the commercial attractions of polythene is the wide range of its applications so that the risk in marketing it is spread. The pattern of applications varies from country to country but the figures published for the U.S.A. are an indication of the way the market may be split in other countries in a few years' time. It is doubtful if Europe will ever be as package conscious as the U.S.A. and polythene film may never account for such a high percentage of the total. Perhaps the use of polythene instead of paper will expand very rapidly in Europe but no doubt a big new application will be something for something not yet thought about. This has been true of every plastics material so far marketed and polythene is not likely to be an exception.

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CHAPTER 32

FUTURE OUTLOOK IN THE U.S.A.

FRAZIER GROFF

THE rapid introduction of polythene into many facets of our everyday life has made most of us conscious of the importance of this material through recognition of its part in the improved quality of goods now obtainable in polythene packages, the more economical and durable housewares now available, better moisture proofing in housing, improved irrigation facilities, flexible cold water pipe, economical and effective bags for clothing and soft goods storage and a host of other items in everyday use. When thinking of the future we are concerned with existing and new types of application fields and to a greater extent with the volume of sales which measures the importance of the application fields. Production capacity, price trends, types of polythene, and factors influencing expansion of sales all add meaning to the picture of the future. Unless attempt is made to predict the future sales with some regard for the course of past expansions in plastics there is likely to be unwarranted optimism over favourable current performance or undue pessimism if current performance is unfavourable. Popular approval of a material is likely to increase the tendency toward optimistic estimates. The expansion of polythene from the beginning of its production (in the U.S.) in 1943 has been rapid and relatively uniform and at this time (1956) suggestions of extremely large future sales are being made. By making an estimate of the near future polythene sales in harmony with the known sales expansion of its closest counterpart and for the more distant future similar to the general performance of older plastics it is hoped that errors due to unwarranted optimism or pessimism will be minimized.

THE FUTURE OF POLYTHENE FROM AN EARLY 1955 VIEWPOINT

During the past few years there have been numerous estimates concerning polythene's current and future market and production capacities. One of these was included in a talk "The Trend of Plastics Use" by Gordon Brown, before a Chemical Marketing Research Association Meeting in New York on May 19th, 1955. In this talk there was a definite market figure for 1954, and an estimate for 1960. This estimate for 1960 is one for which there is evidence of good support. It was based on reliable knowledge of 1954 performance and a detailed investigation into prospective uses and had the merit of being tempered with the suggestion that because of the great vitality of the polythene development the 1960 market figure might be low. The following quotation from Mr.

Brown's talk is of interest and is a good preparation for a new look ahead

"We show 210 million pounds (of polythene) in 1954, and, according to the estimates that have been bringing new producers into the field with such enthusiasm, our 1960 estimate should jump right straight up off the chart. We show a healthy growth to 627 million in 1960, though I must warn in the same breath that this growth is not going to be accomplished with the relatively simple products that have been on the market to date. We believe that polyethylene products will be as numerous as the vinyls or phenolics are today, with each product tailored exactly to a particular process or a particular function. If you questioned us on the markets for polyethylene, most of us would readily admit that 1960 could find a requirement for larger quantities of this product. Every time you turn around, there seems to be a new use of polyethylene, but we of course know about them. We have conducted a great deal of detailed investigation into most of the prospective uses, and these are the conclusions for which we have interesting substantiation. . . . For example, five of our eight selling divisions handle polyethylene. Entirely separately from each other, they have examined the markets natural to them and reached their individual conclusions, which total the 210 million pounds for 1954. Had we gone to our own overall production records and checked that against what we knew of our competitor's activities with respect to capacity as well as manufacture, we would have reached the same figure. We can only hope that 1960 will be equally accurate, though it is interesting that the total comes to far less than the billion pounds per annum so often predicted for this plastic. Indeed, it is even less than the announced capacities that will be in existence before that time.

"The current uses of polyethylene have had so much publicity that we will not take time to enumerate them, but will mention simply that increasing growth is expected in uses for practically every present outlet, with film leading the parade, but with substantial quantities going into coated paper and into the upgrading of wax. That reminds me of one of the markets we analyzed that didn't get dignified with a title of its own, but is a good one to illustrate the statement made previously that in many cases our estimate of the business to be done in 1960 falls far short of the ultimate market. There are two concerns making disposable diapers from polyethylene coated paper and non-woven fabric. You will, no doubt, agree that if they function at all, there should be a ready acceptance amongst young mothers—and fathers. An ultimate market of 131.4 million pounds of polyethylene per year is apparent, but we estimated 1 million pounds for 1960."

HIGH PRESSURE POLYTHENE IN 1956

In the first quarter of 1956 we were aware that between 350 and 400 million pounds of polythene had been sold in 1955 and that in spite of a

production rate of about 480 million pounds per year during the latter part of 1955 there was no oversupply during this period or in early 1956. It also appeared likely that production capacity for high pressure types would total about 600 million pounds per year by the end of 1956* and that further expansion of production capacity for this type material might take place subsequently. The application fields for the high pressure type produced in 1955 were approximately as follows: (1) film and sheeting 37.1%, (2) moulding, 18%, (3) wire and cable insulation 10.9%, (4) pipe 8.3%, (5) coatings 7.7%, (6) bottles 2.6%, (7) miscellaneous 4.0 and export 11.4%.

LOW PRESSURE POLYTHENE

Early in 1955 Phillips Chemical Company announced that they would soon start construction on a plant to produce a "so-called" low pressure polythene by a process which they had patented and that they would license interested companies. Koppers Company also announced that they had obtained a licence to produce low pressure polythene in accordance with the Ziegler patent. Later in 1955 most of the companies then producing high pressure material announced that they were licensed to produce under one or both of the low pressure patents. Several companies not heretofore concerned with polythene production also announced that they were licensed under the Ziegler or Phillips Chemical Company patents. More recently a process by Standard Oil of Indiana has been made available for licence.

The early publicity concerning the new low pressure or high density polythenes suggested that these materials had improved properties and would be cheaper than the high pressure or low density types; however, as added information on the low pressure material was obtained it seemed likely that their manufactured cost would be at least as much as the high pressure types and probably a little more due to higher purification costs. Greater familiarity with the low pressure type makes it appear likely that the two types will complement each other and widen greatly the application fields without notable overlapping. It also appears likely that mixing of the two types will permit the production of a wide range of compounds having closely controlled crystallinity, molecular weight and polymer distribution. It is possible to produce polythenes very similar in properties by the low pressure and the high pressure processes; however the low pressure materials which have been most highly publicized were those of high molecular weight and high crystallinity. Comparison (Table 32.1) between the properties of commercial high pressure low density polythene and the high density highly crystalline low pressure polythene is essential to an understanding of their respective applications.

From Table 32.1 it is evident that the high density polythene will likely find extensive application in rigid pipe, injection moulded articles such as housewares and toys requiring greater rigidity than is obtainable with

* This chapter was written early in 1956, before official statistics for the year were available—*Editor*.

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Table 32.1.—COMPARISON HIGH PRESSURE LOW DENSITY AND LOW PRESSURE HIGH DENSITY POLYTHENES

	High pressure/ low density Type for film	Low pressure/ high density
Density	0.917	0.94-0.96
Softening temp. °C	115	130-138
Tensile strength 25°C lb/sq.in.	1,800	3,000-5,000
% elongation	400	25-400
Modulus at 1% elongation lb/sq.in.	21,000	100,000-150,000
Yield strength at 100°C lb/sq.in.	Approx. 170	Approx. 1,000
% elongation	Approx. 130	Approx. 500
Izod impact ft.lb/in. notch	14	1-5
Instantaneous pipe burst		
@ 20°C lb/sq.in.	1,000	3,900
@ 40°C lb/sq.in.	680	1,200
@ 95°C lb/sq.in.	80	660
Dielectric constant 50 m.c.	2.27	2.34
Dissipation factor 50 m.c.	0.0003	0.0006
Gas permeability (cc) (mil)		
(24 hrs) (100 in. ²) (Atmosphere)		
Oxygen	500	120
Nitrogen	165	32
CO ₂	2,100	475
Moisture transmission (gm) (mil)	22	4
(24 hrs) (metre ²)		
Motor oil permeability	At 30°C and 50°C permeates sufficiently in 2 to 3 days to wet outside of container	Oil does not wet outside of container after several weeks storage at 30°C and 50°C
Environmental stress cracking	Poor to silicone mould release fluid	Better resistance to silicone mould release fluid than film grade low density type

high pressure polythene, material packaging, laminates with paper, foil and Cellophane having superior oil, gas and water vapour permeability. The stiffness of the high density polythene suggests it as a base for printing to replace magazine paper, and for papers where water resistance is important. Very interesting fibres and woven fabrics have been prepared from the high molecular weight highly crystalline low pressure polythenes and the applications in textiles, rope and paper would seem to be very large potential outlets for this material.

Only sample quantities of low pressure polythene were available in 1955 and only very small quantities are expected in commercial channels in 1956. It is expected that 1957 will be the year when low pressure types are commercially available in significant quantities in the United States and it is likely that a production capacity of about 100-150 million pounds per year will be in operation by the end of that year.

EQUIPMENT—SUPPLY AND IMPROVEMENT

The availability of equipment for expansion can of course limit the rate of market expansion of commercial materials. Information published

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in 1956 concerning injection moulding presses and extrusion equipment indicated that expansion of polythene markets would not be hampered by excessively slow delivery of presses, extruders, take-off equipment etc. The time required for injection mould design and construction is always a factor in determining the timing of expanded activities but this type of delay is normal for the plastics industry. Conversations with several equipment manufacturers early in 1956 confirmed the ready availability of equipment at that time and indicated the likelihood of a satisfactory equipment supply for the future.

Improvements made during the last two years in extrusion die design, film take-off equipment and in the commercial electrostatic surface treater for film will in the years immediately ahead most likely result in improved film quality and lower cost finished products. Recent improvements in heat sealing equipment and techniques are also expected to result in lower conversion costs in the future for film and coated products and to open new application fields for these products.

EXPANDING AND NEW APPLICATION FIELDS

Since equipment availability appears satisfactory for rapid polythene expansion, the rate of such expansion depends almost entirely on the broadening of existing applications and the development of new fields. At this time (early 1956) all of the established application fields are expanding in a healthy fashion and many new applications are in early development stages. Some of the new applications though of high capacity may expand initially at a slow rate and have a greater effect on more distant future sales than those of the immediate future.

In the film and sheeting market high capacity fields which may develop rapidly include: continued expansion of produce prepackaging; container liners; overwrapping textiles, soft goods and foods; soil mulches; pond liners; irrigation applications; greenhouse construction; seed packaging and miscellaneous agricultural applications. Applications for film of high potential capacity which may develop more slowly include vapour and moisture barriers in buildings, masonry applications and road construction.

Continuous coated spiral wound tubing and lined convolute tubing for easy opening packages, coated aluminium foil, coated Cellophane, multiwall bags, coated corrugated boxboard for knock down cartons, board coated on both sides for milk and other liquid packaging are all important applications of high potential in the polythene extrusion coatings and laminates fields which should expand rapidly, although the expansion of coated boards and papers may be slowed up somewhat by the necessity for extensive product packaging studies. A very interesting picture of the application fields for polythene extrusion coating was given by Roger A. Calsibet¹ in a talk before the National Flexible Packaging Association on December 8th, 1955.

Wire and cable insulation was one of the early applications for polythene and currently it is an important field (approx. 38 million pounds in 1955)

exhibiting a healthy but not spectacular growth which is expected continue into the future.

The usage of polythene in pipe is sizeable (29 million in 1955) and the rate of sales expansion is high. This rate may be increased by application for rigid pipe and fittings obtainable from high density polythene.

It is likely that the use of thin wall medium and large bottles in liquid packaging may contribute to the existing healthy expansion rate of bottles. Liquid packaging in vacuum formed containers up to 10 gal. size may expand rapidly and if this use were included in the bottle field the expansion rate for the future might be high. Liquid packaging of polythene paced by battery acid packaging looks like an important packaging development with high potential for the future.

The injection moulding of housewares and miscellaneous articles is expanding at a spectacular rate and the advent of high density material should increase this expansion rate. The toy field could become much more important and it is even suggested that high density polythene will invade the field now occupied by high impact polystyrene. It is likely that improvement in the ease of fabrication of toys from miscellaneous moulded parts must precede rapid expansion of polythene in the toy field.

It has been suggested² that polythene fabrications offer satisfactory solution to many of the annoying corrosion problems of today and that its usage in the field of chemical engineering will increase as process engineers become acquainted with the adaptability of this material to their needs. It has been said³ that:

"The recent development of high tensile, high temperature polyethylene introduces a completely new concept in plastic materials of construction. It brings to the fabricator a material having high rigidity, good temperature resistance, high impact strength and extremely good chemical resistance. The HT polyethylenes can replace many of today's more expensive materials and the resulting products will be lower in material cost and need less maintenance.

A major factor in the utilization of HT polyethylenes is their excellent weldability which allows the fabrication of structures and equipment limited only by the imagination."

New and possibly very large application fields for high density polythene as a replacement for paper for magazines and special uses and in fibres and woven fabrics were mentioned previously. These could be very large long term application fields.

Irradiated polythene may extend the application field. Goodwin and Wetzel suggest⁴ special applications for this material in packaging, electrical insulation, housewares and equipment for which un-irradiated polythene is relatively unsatisfactory.

ESTIMATE OF POLYTHENE SALES FOR 1956*

Table 32.2 contains figures for the sales of polythene from 1943 to 1955 inclusive. Running 5 year averages are shown for the various

* Cf. footnote on p. 539.

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periods and these tend to smooth out year to year irregularities. When the running 5 year averages are plotted on a semi-logarithmic scale an essentially straight line for the period 1947 to 1955 inclusive is obtained. If now the actual sales for 1954 and 1955 be plotted (Fig. 32.1) a straight line passing through or close to the plotted point for 1955 seems justified

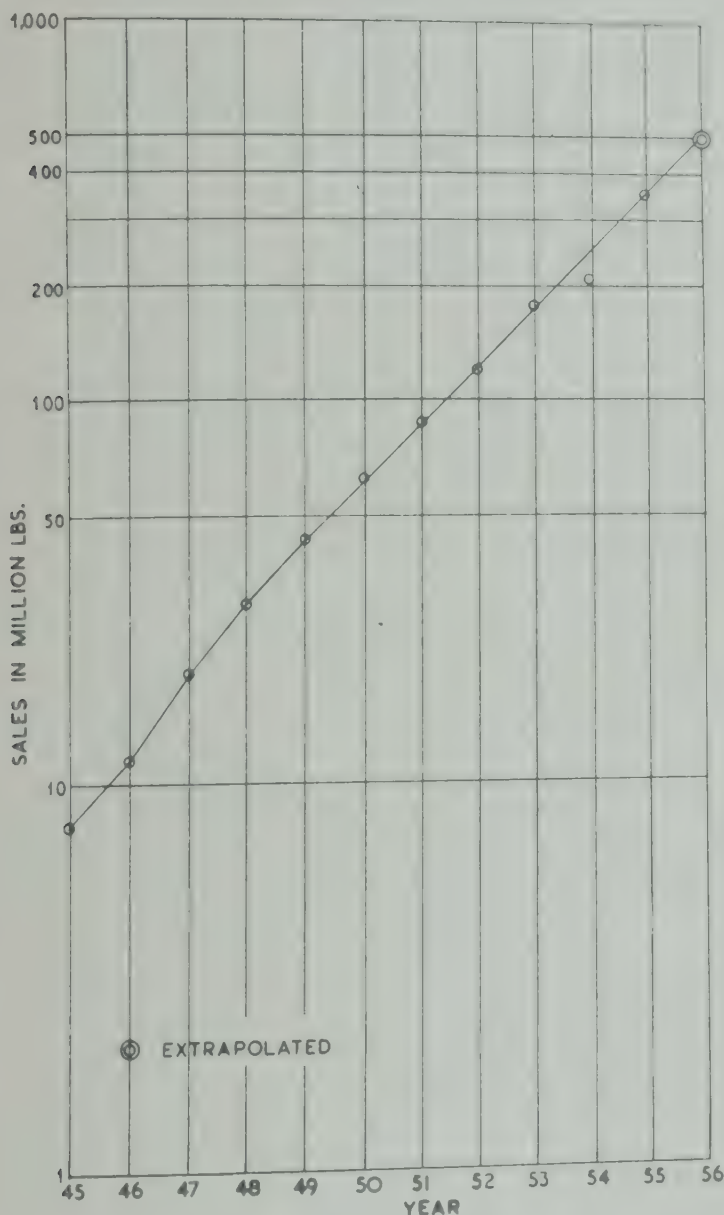


Fig. 32.1. Plot of "running 5 year average" of polythene sales for 1954-55, and actual sales, 1954 and 1955

for the period 1948 to 1955 inclusive. Since we know that late in 1955 polythene was being produced at a rate of 480 million pounds per year and that there was no surplus and that sales in early 1956 were as good or a little better than in late 1955 extrapolation to a sales of 500 million pounds for 1956 seems a reasonable estimate. When production data for

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Table 32.2. POLYTHENE SALES—POUNDS AND YEARLY INCREASE

	Sales, millions of lb	Increase over previous year %	Sales, millions of lb running 5 yr average	Increase over previous year %
1943	1.0		—	
1944	3.0		—	
1945	6.0		7.8	—
1946	13.0	116	11.4	46
1947	16.0	23	19.2	69
1948	19.0	20	29.0	50
1949	42	120	43.4	50
1950	55	31	62.8	45
1951	85	55	86.8	38
1952	115	35	119.8	38
1953	137*	19	179	49
1954	207*	51		
1955	350*	69		

Note: 1943-1952 data—Chemical Economics Handbook—Stanford Research Institute.
Data revised September 1953.

* *Modern Plastics*, Jan. 1956.

Table 32.3. SALES OF THERMOPLASTIC EXTRUSION AND
MOULDING MATERIALS

Year	Sales* (mil- lions of lb)	Calcu- lated sales for indivi- dual years	Average % increase over previous year	Poly- thene sales (mil- lions lb)	Sales of thermoplastics extrusion and moulding materials—less polythene		
					Millions lb	% increase over previous year	Average % increase
1940	20				20	—	
1941		30			30	50	
1942		45	50		45	50	
1943		68		1	67	49	
1944		102		3	99	40	
1945		153		6	147	53	50
1946	239			13	226	58	
1947		282		16	266	18	
1948		333		19	314	17	
1949		393	18	42	351	16	17
1950		463		55	408	13	
1951	554			85	469	19	
1952	571		3	115	456	—1	
1953	675		18	137	538	9	12
1954	730		8	207	523	—1	
1955	1,080		47	350	730	40	

* Data from *Modern Plastics*, 33, 83 (Jan. 1956); original data, U.S. Tariff Commission.

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the period 1943-1954 inclusive from a second source was plotted the extrapolation to 1956 was also 500 million pounds.

ESTIMATING ALL SALES BEYOND 1956

Although extrapolation of the curve in Fig. 32.1 for 10 months seems reasonable for 1956 we know that a slowing down in the sales expansion must occur and a basis for estimating sales in 1957 and beyond must be found unless we just pick the figures out of the air. Up to this time, polythene is used mainly in the form of extrusions and mouldings. Data⁵ from the U.S. Tariff Commission indicate the sales of thermoplastic moulding and extrusion materials from 1940 to 1955 inclusive; the materials included are vinyls, cellulose, polystyrene and polythene and their combined sales increased from 20 million pounds in 1940 to 1,080 million pounds in 1955. The information readily available does not permit close comparison of the application fields covered but it is generally known that the combined fields of application for moulded and extruded polystyrene materials, vinyl resins and cellulose are very similar to the application fields for extruded and moulded polythene.

Table 32.3 shows the sales from 1940 to 1955 inclusive of thermoplastic, extrusion and moulding materials, the sales of polythene, and the sales of thermoplastic extrusion and moulding materials less the sales of polythene materials for that period. When these data are plotted as in Fig. 32.2 curves may be drawn showing the sales expansion of these groups. There is a great similarity in the rate of sales expansion for the combined polystyrene, cellulose and vinyl extrusion and moulding compounds (curve B) and polythene (curve C). The difference between curve A and curve B is small and does not change the general picture. The sales expansion of polythene from a sales volume of 20 million pounds to about 225 million pounds is at approximately the same rate as that of the thermoplastic extrusion and moulding materials. Above a sales volume of 225 million pounds the sales expansion of the thermoplastic extrusion and moulding compounds was slower and continued at the lower rate for a number of years whereas polythene sales expansion above 225 million pounds continued for another year (1955) at the same rate as for previous years. These curves provide the most likely basis for predicting the general course of polythene sales immediately subsequent to 1956 and curves A and B are similar to the data for all plastics which indicate that in the more distant future expansion over sales of the previous year will likely be about 10%.

ESTIMATED SALES 1957-1965

As has been indicated we were aware early in 1956 that in spite of a production rate of 480 million pounds per year during late 1955 there was no over supply of polythene during the latter part of 1955 or early 1956. It was also apparent early in 1956 that there was no shortage. It herefore appears reasonable to expect a sales expansion in 1956 of the

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same order as for previous years and this results in an estimate of million lbs sales for 1956. A comparison of curves B and C in Fig. 32.2 would lead us to expect a drop in the expansion rate of polythene sales in 1956 but in view of actual data from late 1955 and information from the field in early 1956 it was estimated that the drop would not occur until 1957 and that the sales expansion would be 20% for that year.

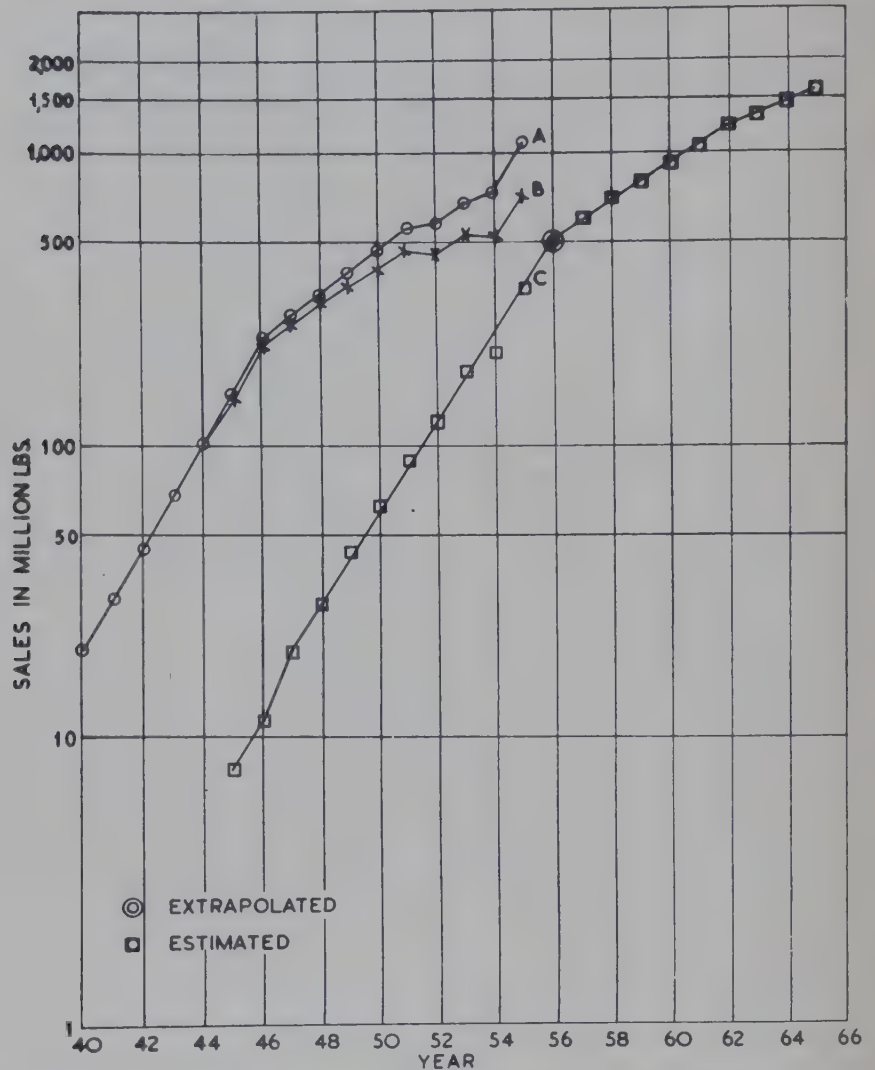


Fig. 32.2. Sales of thermoplastics and polythene. A—All thermoplastic extrusion and moulding compounds; B—all thermoplastic extrusion and moulding compounds less polythene; C—polythene.

15% per year for 1958–62 inclusive, and 10% per year for 1963 to 1965 inclusive.

PRODUCTION CAPACITY 1956–1965

The production capacity for high pressure and low pressure polythene is indicated to some extent in current literature and this information has been used to guide estimates of production capacity for the period 1956 to 1965. Estimates of sales in pounds and production capacity in pounds for 1956 to 1965 inclusive are included in Table 32.4.

FUTURE OUTLOOK IN THE U.S.A.

Table 32.4. ESTIMATED SALES AND CAPACITY OF POLYTHENE 1956-1965
(MILLION LB)

Year	Estimated sales millions of pounds	Estimated production Capacity	
		High pressure	Low pressure
1956	500	600	—
1957	600	600	100
1958	690	650	150
1959	790	700	200
1960	910	750	250
1961	1,045	850	300
1962	1,200	900	400
1963	1,320	950	500
1964	1,455	950	600
1965	1,600	950	800

DISTRIBUTION OF POLYTHENE AMONG APPLICATION FIELDS

The consumption of polythene in end uses for 1955 has been estimated¹⁷ as follows: film 37%, injection moulding 18%, wire and cable 11%, pipe 8%, paper and film coating 8%, bottles and jars 3% and miscellaneous 15%. In 1954 end uses were: film 33%, injection moulding 16%, wire and cable 14%, pipe 10%, paper and film coating 9%, bottles and jars 3% and miscellaneous 15%. It is expected that film will continue to be the volume leader since vigorous expansion is expected in current outlets and impressive new fields for films such as agricultural applications, and construction vapour barriers are in early stages of development. Injection moulded applications should remain in second place in the application volume distribution pattern for the future and their percentage of the total might increase due to the advent of high density polythene which widens the application field for injection moulded articles. In the future about 8%-10% of the total polythene will probably be used in wire and cable and it is expected that this percentage may go down slightly due to the high rate of expansion in the other application fields. Pipe and bottles and jars might gain a little in their percentage of the total at the expense of wire and cable. Vacuum formed containers and miscellaneous shapes, fibres and woven fabric, are expected to increase significantly in volume and it may be necessary to give them a separate place in the distribution pattern of the future. Paper and film coatings should also undergo large expansion. Applications such as disposable diapers, and hospital sheets of non woven fibre coated with polythene could amount to 250 million pounds of polythene per year and extension of the disposable sheet to hotel use and transportation facilities would increase the potential for the sheet application appreciably. The up-grading of Cellophane by coating on two sides with polythene could also become an important future outlet. Polythene consumption by end uses in 1960 might possibly be as follows: film 35%, moulding 22%, wire

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and cable 8%, pipe 11%, paper and film coatings 15%, bottles and jars 5% and miscellaneous including fibre, woven fabrics and structural materials 4%.

PRICE TRENDS

There have been steady reductions in the price of polythene in recent years. Early in 1956 film grade polythene was 41¢. per lb, regular injection moulding grade was 41¢. per lb and black pipe compound was 35¢. per lb. It is expected that the downward trend of prices will continue but when the changes will occur and how large they will be is very uncertain. It is possible for market expansion to keep up with production capacity and prevent a drop in prices but this is likely only for a limited time. The market for polythene could be glutted by over production and a large drop in price result but this also seems unlikely.

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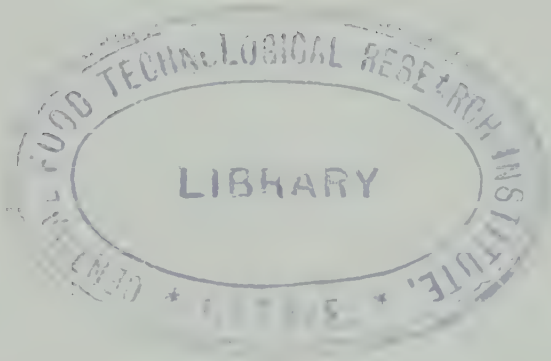
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